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August 15, 2000

Carol Browner, Administrator
US Environmental Protection Agency
P.O. Box 1473
Merrifield, VA 22116
Attention: Chemical Right-to-Know

American Petroleum Institute (API) Petroleum HPV Testing Group

**HPV Registration Number** 

## RE: HPV Test Plan and Robust Summaries Submission for Petroleum Gases

Dear Ms. Browner:

The American Petroleum Institute, on behalf of the Petroleum HPV Testing Group, is pleased to submit the Petroleum Gases Test Plan and Robust Summaries. Our consortium has chosen not to use the HPV Tracker system for submission of our test plans due to the complexity of petroleum substance categories and subsequent test plans. We are therefore submitting the test plan, as well as robust summaries directly to EPA to make available for public comment.

Electronic copies, in .PDF format, of the test plan and robust summaries, are accompanying this letter via email to the EPA HPV robust summary email address (http://www.epa.gov/chemrtk/srbstsum.htm). This submission is also being sent, via email, to Charles Auer.

Please feel free to contact me (202-682-8344; twerdokl@api.org or Tom Gray (202-682-8480; grayt@api.org) with any comments or questions you may have concerning this submission.

Sincerely,

Cc: C. Auer (via email)

T. Gray

# PETROLEUM GASES TEST PLAN

**Submitted to the US EPA** 

by

The American Petroleum Institute Petroleum HPV Testing Group

**Consortium Registration #** 

# PETROLEUM GASES TEST PLAN

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## PETROLEUM GASES TEST PLAN

## PLAIN LANGUAGE SUMMARY

There are 153 HPV substances covered in the Petroleum Gases Test Plan plus 8 similar substances that are not on EPA's 1990 HPV list. These substances come from natural gas processing and petroleum refining operations. Most of the gases are produced as by-products from different processes in the refinery. Many are combined and undergo further processing to remove unwanted impurities before being sold. Others are burned as fuel to operate refinery equipment. In either case, most of these petroleum gases are intermediate process streams that do not leave the refinery. Only a few of the 161 gases in the test plan are sold as finished products.

Although the compositions of these gaseous substances vary widely, they have a finite number of possible constituents. They all contain predominately gases or highly volatile liquids having one to five carbon atoms (C1 to C5) along with inorganic substances such as hydrogen, hydrogen sulfide, carbon monoxide, and ammonia. This is why a single category can encompass this large group of substances. The Petroleum HPV Testing Group will evaluate each of the individual C1 to C4 saturated hydrocarbons (methane, ethane, propane, butane, and isobutane) and a representative commercial sample of liquefied petroleum gas (LPG). This information will be combined with existing data on the inorganic substances and data that are being developed by other consortia in the HPV Challenge or through other mechanisms (OECD, ICCA, or EPA test rule) to develop a complete hazard evaluation of all the substances in the Petroleum Gases Test Plan.

Much is already known about how simple petroleum gases affect the body. The lighter gases (methane and ethane) are considered simple asphyxiants which means that at low concentrations they do not cause harmful effects. At very high concentrations however, they displace oxygen in the air and reduce the amount available for breathing. Prolonged exposure at these concentrations can cause asphyxiation (or suffocation) from lack of oxygen. The heavier gases (propane and butanes) can also act as asphyxiants but also have a mild depressant effect on the nervous system. Symptoms of overexposure can include shortness of breath, drowsiness, headaches, confusion, and decreased coordination. These symptoms are reversible if exposure is stopped. At the concentrations required to cause effects these gases also present an explosive hazard, so exposure to these levels is rare.

Because these gases can directly or indirectly (as an asphyxiant) affect the nervous system, the simple gases (ethane, propane, butane, and isobutane) will be tested to determine what concentrations do have an effect. This will be done in animal studies using high concentrations for short durations. Because of the flammability hazard, the concentrations used will be limited to one-half the lower explosive limit of the gas. All the gases except methane will also be tested in studies lasting 28 days to determine whether prolonged exposures can affect any of the body's organ systems. Methane is not being tested because its known to be present at high concentrations in intestinal gases. In addition, longer-term (90-day) studies will be done with the LPG, using more specialized techniques to detect possible nervous system harm.

Many of the individual gases have already been tested in studies using bacteria for their ability to alter DNA, and were found to be negative. No studies have been done to look for DNA alterations in animals exposed to the gases, so these studies will be done using the individual gases as well as the LPG sample. Animal studies will also be done on the individual gases to determine their ability to cause adverse reproductive effects and effects on the developing fetus. The LPG sample will be evaluated in specialized studies to detect the possibility of birth defects.

Because these materials are gases they will disperse to the atmosphere if released into the environment. They would not be expected to contaminate water, accumulate in the soil, or adversely affect plant life. For that reason, no aquatic or other environmental effects studies are planned. Information on their environmental fate may be developed if appropriate.

## **DESCRIPTION OF THE PETROLEUM GASES CATEGORY**

The 161 substances in the Petroleum Gases Test Plan are gases or highly volatile liquids at standard temperature and pressure. A few of the substances are pure compounds such as *Propane* and *Butane*, but most are variable complex substances. The convention for assigning CAS names to these substances is usually based on last process step, e.g., *Tail gas (petroleum), gas recovery plant dethanizer*, but in some cases, the names are based on a general chemical description, *e.g.*, *Hydrocarbons*, *C2-4*, *C3-rich*. Appendix 1 provides a complete listing of substances included in this Test Plan. These gaseous materials are Class II substances on the Toxic Substances Control Act (TSCA) Chemical Inventory. Class II substances are, "Chemical Substances of Unknown or Variable Composition, Complex Reaction Products, and Biological Materials."

Analytical capabilities allow determination of the complete composition of gas streams containing hydrocarbons C5 and lighter, plus incidental gases such as hydrogen sulfide, ammonia, carbon monoxide, carbon dioxide, and hydrogen. The status of gas streams with respect to TSCA, therefore, could be determined by identification of the individual components present. This approach was adopted in the joint API/EPA preparation of Addendum I to the TSCA Inventory in January 1978. Therefore, numerous gas streams were reported for the TSCA Inventory and have been used by manufacturers in their Inventory Update Rule (IUR) submissions ever since.

The Petroleum HPV Testing Group has coordinated its efforts with other testing consortia to avoid duplication of effort on this large and complex set of substances. To that end, the substances in this test plan are primarily produced either in petroleum refineries as the light end fractions of distillation and cracking processes, or in gas plants that separate natural gas and natural gas liquids. Other consortia (see Test Material Justification and Description for more details) are submitting complementary test plans.

## **Classification of Petroleum Gases**

The Petroleum HPV Testing Group has used the same categorization of petroleum substances that has been adopted by the European Union (EU) in their legislation (Official Journal of the European Communities, L84 Volume 36, 5 April 1993. *Council Regulation (EEC) No 793/93 of 23 March 1993 on the evaluation and control of risks of existing substances*). Adoption of this existing categorization facilitates international harmonization of classification of these complex chemical substances of variable composition. Additionally, use of the same categories will also facilitate coordination of efforts to summarize existing data and develop new hazard data that will be appropriate for hazard and risk characterization worldwide and, therefore, avoid unnecessary duplication of testing.

The petroleum gases in this test plan fit into one of two EU categories for petroleum substances as follows:

## Petroleum Gases (Category 2)

Streams obtained from crude oil distillation, cracking processes, and tail gases containing saturated and/or olefinic hydrocarbons, mainly in the range  $C_2$  to  $C_5$ , including liquefied gases (predominantly propane and butane).

## Refinery Gases (Category 35)

Streams obtained from various processes and containing  $C_1$  to  $C_5$  hydrocarbons, together with significant concentrations of other gases, such as hydrogen, nitrogen, hydrogen sulfide, carbon monoxide, etc.

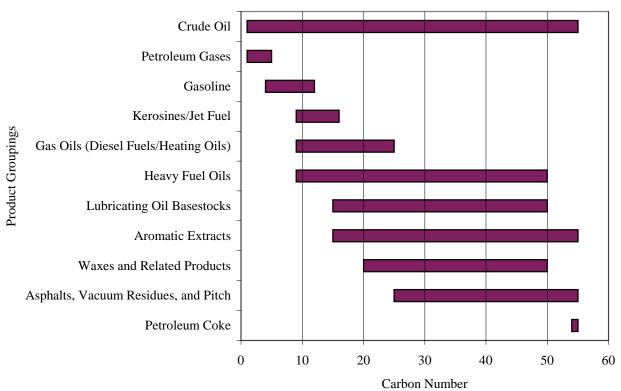
Because the EU categories do not include substances from natural gas and gas liquids processing, several additional HPV chemicals were placed into the appropriate category. This was simple to accomplish because the hydrocarbon and inorganic constituents are identical to those found in the EU categories; only the origin of the substances is different. This will not affect the hazard assessment of these substances.

## **Petroleum Refining**

Petroleum, or crude oil, is an extremely complex substance. The hydrocarbon molecules may include from one to 50 or more carbon atoms. At room temperature, hydrocarbons containing one to four carbon atoms are gases; those with five to 19 carbon atoms are usually liquids; and those with 40 or more carbon atoms are typically solids. The refining process uses distillation as well as chemical treatment, catalysts, and pressure to separate and combine the

basic types of hydrocarbon molecules into petroleum "streams" which have the characteristics needed for blending commercial petroleum products. Distillation is not a precise procedure and refining processes vary from refinery to refinery. As a consequence there is not a sharp cut-off between each of the streams that have been separated, and this results in an overlap of substances that occurs in each of the streams. The overlap of substances that occurs between petroleum gases, gasoline, kerosine/jet fuel, gas oils, and heavy fuel oils is solely attributable to the process of separation by distillation. Figure 1 below shows the typical carbon chain lengths found in various petroleum product groupings and clearly demonstrates the overlap of substances that occurs. Overlap between petroleum gases and gasoline begins with compounds of carbon chain lengths four and greater. Compounds with carbon chain lengths of six and greater (up to twelve) are predominantly found in gasoline.

Figure 1.



Numerous refinery processes produce gaseous streams. These include primary distillation, catalytic cracking, catalytic reforming, hydrocracking, hydrodesulfurization, hydrotreating, isomerization, polymerization, sweetening, and thermal cracking. An analysis of gaseous streams from a representative USA refinery is contained in Appendix 2. The key findings of these analyses were the following:

Refinery gas streams have a limited number of constituents; Compositions vary widely from stream-to-stream and sample-to-sample; CAS numbers and TSCA Inventory descriptions do not specify exact composition;

The Test Material Justification and Description section of this Test Plan will use these key findings to outline an efficient testing strategy for all 161petroleum gases.

## **Commercial Gas Processing**

Production of natural gas involves separation of methane (the principle component of commercial natural gas) from other hydrocarbons called natural gas condensate. Separation of the gaseous products is done in a processing facility commonly called a "gas plant." The condensate is treated to remove undesirable components such as

hydrogen sulfide and mercaptans (a process called "sweetening") and fractionated into commercial Liquefied Petroleum Gas (LPG) products.

Natural gas and LPG are the most familiar substances in the Petroleum Gases Test Plan. LPG is predominantly a mixture of C3 and C4 hydrocarbons with potentially small amounts of other hydrocarbons in the C1-C2 and C5-C7 range. Liquefaction of these gases occurs by application of pressures of a few atmospheres, which enables them to be conveniently stored and transported in light pressure vessels. There are four LPG mixtures with specifications established by the American Society for Testing and Materials (ASTM); none of them are associated with a specific CAS number. Complete specifications can be found in ASTM D 1835.

## The four are:

- 1. <u>Commercial Propane</u> is the preferred fuel type for domestic, commercial, and industrial fuels. It is also a suitable fuel for low severity internal combustion engines. The composition is predominantly propane and/or propylene. The maximum vapor pressure at 100F is 208 psig. It usually contains less than 2.5% of butane and heavier materials.
- 2. <u>Commercial Butane</u> is used principally as feedstock for petrochemicals, synthetic rubber, and as blending stocks or feedstock in the manufacture of motor gasoline. Its use as a fuel is generally limited to industrial applications where vaporization problems are not encountered; however, small quantities are used as domestic fuel. The composition is predominantly butanes and/or butylenes. The maximum vapor pressure at 100F is 70 psig. It usually contains less than 2.0% pentanes and heavier materials.
- 3. <u>Commercial Butane-Propane Mixtures</u> cover a broad range of mixtures, which permits the tailoring of fuels or feedstock to specific needs. The composition is predominately mixtures of butanes and/or butylenes with propane and/or propylene. The maximum vapor pressure at 100F is 208 psig. The mixture usually contains less than 2.0% pentanes and heavier materials.
- 4. <u>Propane HD-5</u> is less variable in composition and combustion characteristics than other products covered by the specifications. It is also suitable as a fuel for internal combustion engines operating at moderate to high engine severity. The composition is not less than 90% propane and not more than 5% propylene. The maximum vapor pressure at 100F is 208 psig. It usually contains less than 2.5% of butane and heavier materials.

The hydrocarbons in the natural gas condensate that are C5 and greater are typically referred to as "natural gasoline." This is typically sold to refineries that process it along with crude oil. Natural gasoline will be included in the Test Plan for Gasoline in 2001.

## **Chemical Composition**

While the composition of substances within the Petroleum Gases Test Plan vary widely from stream-to-stream and even from sample-to-sample, they have a finite number of possible hydrocarbon constituents. Table 1 presents the principle hydrocarbons that make up these substances.

Table 1 Hydrocarbon Constituents Found in Petroleum Gases

One Carbon	Two Carbons	Three Carbons	Four Carbons	Five Carbons
Methane*	Ethane*	Propane*	Butane*	Pentane*
	Ethylene*	Propylene*	Propane, 2-methyl*	Butane, 2-methyl*
	Ethyne	Propadiene	1-Butene*	Butane, 3-methyl
			2-Butene*	1-Pentene
			Propene, 2-methyl*	cis-2-Pentene
			1,2-Butadiene	trans-2-Pentene
			1,3-Butadiene	1-Butene, 2-methyl
				1-Butene, 3-methyl
				2-Butene, 2-methyl
				1,2-Pentadiene
				1-cis-3-Pentadiene
				1-trans-3-Pentadiene
				1,4-Pentadiene
				2,3-Pentadiene
				1,2-Butadiene, 3-
				methyl
				1,3-Butadiene, 2-
				methyl
				Cyclopentane
				Cyclopentene
				Cyclopentadiene

<sup>(\*)</sup> Indicates constituents in the greatest abundance in the Petroleum Gases

Many of the individual hydrocarbons found in the substances in the Petroleum Gases Test Plan are on EPA's HPV chemical list. Table 2 shows the basic hydrocarbon type of these components.

Table 2
Individual HPV Substances<sup>1</sup> in Refinery and Gas Processing Streams

Carbon	Paraffins	Iso-	Cyclo-	Mono-	Di-Olefins	Cyclo-
Number		<b>Paraffins</b>	paraffins	Olefins		Olefins
1	Methane*					
2	Ethane*			Ethylene*		
3	Propane*			Propylene*		
4	Butane*	Propane, 2- methyl*		1-Butene*	1,3-Butadiene	
		-		2-Butene*	1,2-Butadiene	
				Propene, 2- methyl*		
5	Pentane*	Butane, 2- methyl*	Cyclopentane	1-Pentene	1,3-Butadiene, 2-methyl	Cyclopentene
				2-Butene, 2- methyl		

<sup>(\*)</sup> Indicates constituents in the greatest abundance in the Petroleum Gases

The are also several constituents found in the substances in the Petroleum Gases Test Plan that are not hydrocarbons. The inorganic substances, hydrogen, ammonia, hydrogen sulfide, carbon monoxide, and carbon dioxide, can be

<sup>1.</sup> On EPA list hpv90\_2-29-00

found in significant concentrations. In addition, the mercaptans, methanethiol and ethanethiol, are often present. The inorganic substances are not HPV chemicals, while the two mercaptans are HPV chemicals that have been sponsored by the Mercaptans/Thiols Council.

## TEST MATERIAL JUSTIFICATION AND DESCRIPTION

This test plan will take advantage of the fact that there are a limited number of potential constituents within the 161 substances covered by the Petroleum Gases Test Plan. The testing strategy of the Petroleum HPV Testing Group is to evaluate several individual hydrocarbons and a representative LPG. This information will be combined with existing data on inorganic substances and data being developed by other consortia to complete the hazard evaluation. The American Chemistry Council (formerly, Chemical Manufacturers Association) Olefin's Panel, the American Chemistry Council Hydrocarbon Solvent's Panel, and the Mercaptan/Thiol Council are all developing data relevant to the evaluation of the 161 substances in this test plan. Other substances are already part of the OECD/SIDS program. Table 3 outlines the distribution of responsibility for developing information on the individual constituents.

Table 3
Distribution of Responsibility Relevant to the Petroleum Gases Test Plan

Petroleum HPV Testing Group	Olefins Panel	Hydrocarbon Solvents Panel	Mercaptans/ Thiols Council	OECD/SIDS Program	EPA Test Rule on HPV Chemicals
Methane*	Propylene*	Butane, 2-methyl*	Methanethiol	Ethylene*	1,2-butadiene
Ethane*	1-Butene*	Cyclopentane	Ethanethiol	1,3-Butadiene	1-Pentene
Propane*	2-Butene, 2- methyl			2-Butene*	
Butane*				Propene, 2- methyl*	
Propane, 2-methyl*				Pentane*	
Sweetened LPG					

<sup>(\*)</sup> Indicates constituents in the greatest abundance in the Petroleum Gases

The Petroleum HPV Testing Group is responsible for the following materials:

CAS Number	HPV Chemical
74-82-8	Methane
74-84-0	Ethane
74-98-6	Propane
106-97-8	Butane
78-78-4	Propane, 2-methyl
68476-86-8	Sweetened LPG (conforming to ASTM D 1835 specifications for Commercial Butane-
	Propane Mixtures as well as EU requirements)

By taking this approach we not only satisfy the HPV Challenge requirements for the individual HPV substances, but also evaluate the potential extremes of composition for all 161 substances in the Petroleum Gases Test Plan. The samples used to test the individual gases will be of very high purity (>98%). The Sweetened LPG sample will be representative of commercially available LPG that conforms to recognized specifications. These studies will provide a sound scientific basis for judging the toxicity of gases commonly sold to consumers. Because the results of the studies on LPG will be used to support voluntary risk assessments for petroleum substances having widespread use in the EU, the sample used will meet not only ASTM specifications but applicable EU requirements as well.

## EVALUATION OF EXISTING HEALTH EFFECTS DATA AND PROPOSED TESTING

As noted in the Test Material Justification and Description, the testing strategy is to evaluate several individual hydrocarbons and a representative complex substance. This will be accomplished by developing data for needed mammalian toxicity endpoints for the major alkane constituents of petroleum gases (ethane, propane, and butane), the major isoalkane constituent (2-methylpropane), and a representative sample of Liquefied Petroleum Gas (LPG). Detailed summaries of the available toxicology data, in the form of the Robust Summaries, are included in this test plan (Appendix 3.). The additional toxicology testing to be conducted is summarized in the Matrix of Available Adequate Data and Proposed Testing. Because of the vapor pressure of the test materials at standard temperature and pressure, inhalation is the only route of exposure that will be evaluated.

Much is already known about the toxicity of petroleum hydrocarbon gases, both from industrial experience as well as their historical use as anesthetic gases. The lighter gases (methane and ethane) are considered simple asphyxiants which means that at low concentrations they do not cause harmful effects. At very high concentrations however, they displace oxygen in the air and reduce the amount available for breathing. Prolonged exposure at these concentrations can cause asphyxiation (or suffocation) from lack of oxygen. The heavier gases (propane and butanes) can also act as asphyxiants but also have a mild depressant effect on the nervous system. Symptoms of overexposure can include shortness of breath, drowsiness, headaches, confusion, and decreased coordination, and are reversible if exposure is stopped. At the concentrations required to cause effects these gases also present an explosive hazard, so exposure to these levels is not common

Since hydrocarbon gases are generally exhaled unchanged after absorption, it could be argued that additional testing would provide little additional information on the potential toxicity of C1-C4 hydrocarbon gases. Nevertheless, evaluation of the simple hydrocarbon gas components is an important part of the overall effort required by the various groups participating in the HPV Challenge. A systematic and thorough evaluation of the individual components is necessary to ensure that accurate information is available to assess the potential hazards of the 161 substances being addressed by this plan.

## **Acute Toxicity**

Although the acute toxicity of these hydrocarbons is considered to be negligible, there are no recently conducted studies done according to current guidelines.  $LC_{50's}$  in rats were >800,000 ppm for propane exposure for 15 minutes, >570,000 ppm for isobutane exposure for 15 minutes, and 276,000 ppm for butane exposure for 4 hours. The  $EC_{50}$  for central nervous system (CNS) depression was reported to be 280,000 ppm after a 10-minute exposure of rats to propane. However, isobutane was reported to cause CNS stimulation in rats with an  $EC_{50}$  at levels of 200,000 ppm for 10 minutes. Petroleum gases have been reported to sensitize the heart to epinephrine in experimental animals at levels of 70,000 ppm. While no specific studies were located, petroleum gases are generally not considered to be eye or skin irritants in their gas or vapor form, however as liquids, they can cause frostbite. The American Conference of Governmental Industrial Hygienists (ACGIH) considers methane and ethane to be simple asphyxiants. Occupational exposure standards have been established by ACGIH for propane, butane, and LPG based on asphyxiation and CNS effects.

Summary: The saturated hydrocarbon components of petroleum gases are simple asphyxiants and may have some CNS effects at very high levels, which would generally only be encountered during large, catastrophic, accidental releases or in enclosed spaces. All of the toxicological effects cited above occurred at concentrations well above the lower explosive limit for these materials. While the available acute toxicity studies were not GLP and have marginal to unacceptable reliability per evaluation criteria, only limited additional testing is planned. This testing will focus on evaluating the potential CNS effects of ethane, propane, butane, isobutane, and sweetened LPG at concentrations up to 50% of the lower explosive limits.  $LC_{50}$  values will be estimated from these studies.

## **Repeated Dose Toxicity**

A repeated dose inhalation study was conducted using male and female rats exposed to 50:50 mixtures of either n-butane/n-pentane or isobutane/isopentane for the purpose of examining possible nephrotoxic effects. Exposure was

for 6 hours/day 5 days/week for 90 days. Necropsies were performed on one-half of the male rats after the twentieth exposure. Exposure levels were 0, 1017, and 4489 ppm. After gross necropsy of all tissues for the presence of lesions and other abnormal conditions only liver and kidney weights were determined. All major tissues were collected and fixed, but only kidneys were examined histologically. Body weights, taken weekly, were statistically decreased compared to control by weeks 3 and 4 in both sexes. These effects were reversed in male rats but not female rats by the end of the study. A slight nephrotoxic response observed at the interim examination was not observed at the end of the study. The NOAEL was 4489 ppm for 90 days. Although a GLP study, the limitations of this study were the lack of complete histological examinations of tissues, including reproductive organs, and the lack of clinical chemistry and hematological analyses. No effects were observed at ~1/4 the Lower Explosive Limit (LEL) of these chemicals, suggesting that higher doses need to be tested.

Summary: There is only limited information available on petroleum gases using repeated dose studies. The individual gases (with the exception of methane) will be tested using the 28-day repeated dose inhalation study protocol (OECD 412). Because methane is a metabolic product of intestinal bacteria in humans and intestinal gas can be up to 20% methane, no toxicology studies are needed on methane. Because the greatest likelihood of potential exposure to the population at large is expected be to commercial petroleum gas products for longer periods of time, the LPG sample will be tested using a 90-day repeated dose inhalation protocol (OECD 413) that will include neurotoxicity evaluations.

## **In Vitro Genetic Toxicity**

A number of petroleum gases have been tested for bacterial mutagenicity using the Ames Assay with *Salmonella typhimurium* strains TA98, TA100, TA1535, TA1537, and TA1538 with and without metabolic activation. Modified test protocol OECD 471 was used to test the gaseous substances at levels of 5, 10, 20, 30, 40, and 50% in air. The six gases tested were predominantly (i.e., >96%) propane, n-butane, two isobutanes, n-pentane, and isopentane. Positive controls were included in the study. Toxicity to some of the gases, but not mutagenicity, was observed. Mutagenicity was not observed when the gases were retested at lower, non-toxic levels.

Summary: Propane, n-butane, isobutane, n-pentane, and isopentane were not mutagenic with or without metabolic activation. On this basis, only the representative LPG sample will be tested using the Ames Assay (OECD 471).

## In Vivo Genetic Toxicity

No useable *in vivo* genetic toxicity data was identified.

Summary: No data was found. On this basis, all test substances in this category (except methane) will be tested using a mammalian genetic toxicity protocol, OECD 474 (micronucleus assay) conducted by inhalation.

## **Reproductive and Developmental Toxicity**

No useable reproductive or developmental toxicity test data were identified.

Summary: Because of the lack of test data, all individual gases (except methane) and the LPG stream will be tested using reproductive and developmental protocols. The individual gases of this category will be tested using the combined reproduction/developmental testing protocol (OECD 421) conducted by inhalation exposure. Because the greatest likelihood of potential exposure to the population at large is expected to be to mixed petroleum gas streams for longer periods of time, the LPG stream will be tested for developmental toxicity (OECD 414) using inhalation exposures.

# EVALUATION OF EXISITING PHYSICOCHEMICAL AND ENVIRONMENTAL FATE DATA AND PROPOSED TESTING

The physicochemical endpoints in the HPV chemicals program include:

Melting Point Boiling Point Final 08/15/00 Consortium #

Vapor Pressure Octanol/Water Partition Coefficient Water Solubility

The environmental fate endpoints include: Photodegradation Stability in Water (Hydrolysis) Transport and Distribution (Fugacity) Biodegradation

## **Physicochemical Data**

Available data on methane, ethane, propane, butane, and 2-methylpropane are in the robust summaries for these materials. The range of values for these chemicals will cover the substances in this testing plan. For those substances with inorganic constituents like hydrogen sulfide or carbon monoxide, their physicochemical properties may be influenced by the quantity of inorganic present. Where appropriate, data for these constituents will be added to the robust summaries.

In addition to existing information, physicochemical data for methane, ethane, propane, butane, and 2-methylpropane will be developed using sources recommended by EPA. There are estimation models (Structure-Activity Relationships, SAR) for each of these endpoints in the EPIWIN (1) (Estimation Program Interface for Windows) computer program and EPA has indicated that it will accept estimated data using this program (2).

Summary: Where measured values are not available from the literature for methane, ethane, propane, butane, and 2-methylpropane, we will calculate physicochemical data as described in the EPA document titled, *The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program* and add them to the robust summaries.

## **Environmental Fate Data**

Calculated atmospheric half-lives for methane, ethane, propane, butane, and 2-methylpropane are in the robust summaries for these materials. The fugacity modeling supports the position that data on other environmental fate processes (e.g., biodegradation and hydrolysis) will either be much less or not relevant when assessing the fate of Petroleum Gases. Predictive computer models will be used to develop meaningful environmental fate data for chemicals that are gaseous at relevant environmental temperatures and pressures. Although there are some data for the Petroleum Gases category, additional information will be prepared.

The following describes the fate endpoints and the type of data/information that will be developed.

**Photodegradation:** Direct photochemical degradation occurs through the absorbance of solar radiation by a chemical substance. If the absorbed energy is high enough, the resultant excited state of the chemical may undergo a transformation. Simple chemical structure can be examined to determine whether a chemical has the potential for direct photolysis in water. First order reaction rates can be calculated for some chemicals that have a potential for direct photolysis using the procedures of Zepp and Cline (4).

Photodegradation can be measured (3) (EPA identifies OECD test guideline 113 as a test method) or estimated using computer models accepted by the EPA (2). An estimation method accepted by the EPA includes the calculation of chemical specific atmospheric oxidation potentials (AOP). Atmospheric oxidation can occur as a result of hydroxyl radical attack. This reaction is not direct photochemical degradation, but rather indirect degradation and can be calculated using a computer model. Chemicals that are gases will be available for atmospheric oxidation reactions with photochemically generated hydroxyl radicals. This will be the most significant route of degradation in the environment for the chemical components comprising Petroleum Gases.

Although there are data for photodegradation in the robust summaries for methane, ethane, propane, butane, and 2-methylpropane, their quality cannot be confirmed. Therefore, relevant atmospheric degradation data will be calculated using the computer program AOPWIN (1). This program calculates a chemical half-life based on an

overall OH reaction rate constant during a 12-hr day and a standard OH concentration (a 12-hr period is used because this reaction occurs during daylight). This calculation will be performed for methane, ethane, propane, butane, and 2-methylpropane.

Summary: Because of the reliability of available data, we will calculate atmospheric oxidation potential data for methane, ethane, propane, butane, 2-methylpropane.

**Stability in Water:** Hydrolysis of an organic chemical is the transformation process in which a water molecule or hydroxide ion reacts to form a new carbon-oxygen bond. Chemicals that have a potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters (5). The chemical components that comprise the Petroleum Gases category are hydrocarbons, which are not included in these chemical groups, and they are not subject to hydrolysis reactions with water.

Stability in water can be measured (3) (EPA identifies OECD test guideline 111 as a test method) or estimated using computer models accepted by the EPA (2). HYDROWIN (aqueous hydrolysis rate program for Microsoft windows) (1) is an estimation method accepted by the EPA that can be used to calculate hydrolysis rate constants for esters, carbamates, epoxides, halomethanes, and selected alkylhalides. It will not be necessary to run the model for the chemical components in this category because they do not fall within these chemical groups. Instead, a technical discussion as to why these chemicals are not subject to hydrolysis will be prepared.

Summary: Hydrolysis testing and computer modeling will not be conducted for materials in the Petroleum Gases category because they do not undergo hydrolysis. Instead, a technical discussion on the potential for methane, ethane, propane, butane, and 2-methylpropane to hydrolyze will be prepared and added to the robust summaries.

Chemical Transport and Distribution in the Environment: Fugacity based multimedia modeling can provide basic information on the relative distribution of chemicals between selected environmental compartments (i.e., air, soil, sediment, suspended sediment, water, and biota). The US EPA has acknowledged that computer modeling techniques are an appropriate approach to estimating chemical partitioning (fugacity is a calculated endpoint and is not measured).

A widely used fugacity model is the EQC (Equilibrium Criterion) model (6). EPA cites the use of this model in its document titled *Determining the Adequacy of Existing Data* (3), which was prepared as guidance for the HPV chemical program. In its document, EPA states that it accepts Level I fugacity data as an estimate of chemical distribution values. The EQC Level I is a steady state, equilibrium model that utilizes the input of basic chemical properties including molecular weight, vapor pressure, and water solubility to calculate distribution within a standardized regional environment. This model will be used to calculate distribution values for methane, ethane, propane, butane, and 2-methylpropane. A computer model, EPIWIN - version 3.02 (1), will be used to calculate the properties needed to run the Level I EQC model.

Summary: Because of the reliability of existing data, we will calculate fugacity data for methane, ethane, propane, butane, and 2-methylpropane.

**Biodegradation:** Biodegradation is the utilization of a chemical by microorganisms as a source of energy and/or carbon. The chemical is broken down to simpler, smaller chemicals, which are ultimately converted to an inorganic form such as carbon dioxide, nitrate, sulfate, and water. Assessing the biodegradability of chemicals using a standard testing guideline can provide useful information for evaluating chemical hazard.

Products in this category are gaseous. Standard OECD biodegradation test methods are either ill designed or not capable of assessing the relative biodegradability of gaseous materials. Although there are data in the biodegradation robust summaries for methane, ethane, propane, butane, and 2-methylpropane, their quality cannot be confirmed. To provide relevant information for this endpoint, a discussion will be developed on the physical nature of these compounds and the fact that their primary route of loss will be to the air compartment where they will degrade through hydroxyl radical attack (see photodegradation above).

Summary: Because biodegradation is an unlikely fate and available test methods are unsuitable for gases, we will instead prepare a technical discussion on the potential for methane, ethane, propane, butane, and 2-methylpropane to degrade through physical and biological processes.

## EVALUATION OF EXISITING ECOTOXICITY DATA AND PROPOSED TESTING

The environmental effects endpoints in the HPV Challenge program include:

Acute Toxicity to Fish Acute Toxicity to Aquatic Invertebrates Toxicity to Algae (Growth Inhibition)

Measured aquatic toxicity data do not exist for chemicals or products that are included in the Petroleum Gases category. EPA identifies the following test methods to determine these endpoints: OECD Guideline 203, Fish Acute Toxicity Test; Guideline 202, Daphnia sp., Acute Immobilization Test; and Guideline 201, Alga Growth Inhibition Test (3). However, these test guidelines were not designed to assess the acute toxicity of gaseous products like those in the Petroleum Gases category.

As discussed above, the partitioning behavior of the principal hydrocarbon components of Petroleum Gases in the environment suggests that exposure of organisms in aquatic environments to methane, ethane, propane, butane, and 2-methylpropane will be extremely limited. Therefore, fish, aquatic invertebrate, and alga toxicity studies will not be conducted. Instead, a technical discussion will be developed that addresses the physical nature of these substances as well as the fact that the primary compartment to which these products will partition is the air. This statement will include a discussion of calculated aquatic toxicity data for methane, ethane, propane, butane, and 2-methylpropane. The calculated data will be developed using ECOSAR, a SAR program found in EPIWIN (1).

Summary: No ecotoxicity testing will be conducted. Instead, a discussion of the potential aquatic toxicity of methane, ethane, propane, butane, and 2-methylpropane using modeled data will be prepared and included in the robust summaries.

## MATRIX OF AVAILABLE ADEQUATE DATA AND PROPOSED TESTING

Test Material Name CAS #	Methane 74-82-8	Ethane 74-84-0	Propane 74-98-6	Butane 106-97-8	Isobutane 75-28-5	Sweetened LPG 68476-86-8
Melting Point	Adequate	Adequate	Adequate	Adequate	Adequate	С
Boiling Point	Adequate	Adequate	Adequate	Adequate	Adequate	С
Vapor Pressure	Adequate	Adequate	Adequate	Adequate	Adequate	С
Partition Coefficient	Model	Model	Model	Model	Model	С
Water Solubility	Model	Model	Model	Model	Model	С
Photodegradation	Model	Model	Model	Model	Model	С
Stability in Water	N/A	N/A	N/A	N/A	N/A	N/A
Transport and Distribution	Model	Model	Model	Model	Model	С
Biodegradation	N/A	N/A	N/A	N/A	N/A	N/A
Acute Toxicity to Fish	N/A	N/A	N/A	N/A	N/A	N/A
Acute Toxicity to Aquatic Invertebrates	N/A	N/A	N/A	N/A	N/A	N/A
Toxicity to Algae	N/A	N/A	N/A	N/A	N/A	N/A
Acute Inhalation	С	Test	Test	Test	Test	Test
Repeated Dose	С	Test	Test	Test	Test	Test
Genotoxicity, bacterial	C	С	Adequate	Adequate	Adequate	Test
Genotoxicity, in vivo	C	Test	Test	Test	Test	Test
Repro/Developmental	C	Test	Test	Test	Test	Test

Adequate Indicates adequate existing data Test Indicates proposed testing

Model Indicates data will be obtained with EPA approved models
C Indicates category read-across from existing or proposed test data

N/A Indicates that evaluation of endpoint is Not Applicable due to physical-chemical state or route of

administration. Technical discussions will be developed to address these endpoints as appropriate.

## **REFERENCES**

- 1. EPIWIN. 1999. Estimation Program Interface for Windows, version 3.02. Syracuse Research Corporation, Syracuse, NY, USA.
- 2. US EPA. 1999. The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program. OPPT, EPA.
- 3. US EPA. 1999. Determining the Adequacy of Existing Data. OPPT, EPA.
- 4. Zepp, R. G., and D. M. Cline. 1977. Rates of Direct Photolysis in the Aqueous Environment. Environ. Sci. Technol. 11:359-66
- 5. Neely, W. B. 1985. Hydrolysis. In: W. B. Neely and G. E. Blau, eds. Environmental Exposure from Chemicals. Vol I., pp. 157-173. CRC Press, Boca Raton, FL, USA.
- 6. Mackay, D., A. Di Guardo, S. Paterson, and C. E. Cowan. 1996. Evaluating the Environmental Fate of a Variety of Types of Chemicals Using the EQC Model. Environ. Toxicol. Chem. 15:1627-1637.
- 7. American Society for Testing and Materials, D 1835 91. Standard Specification for Liquefied Petroleum (LP) Gases.

## **APPENDIX 1**

## Petroleum Gases Category Constituents by CAS No.

## **EU Category**

Petroleum Gases (Category 2)

CAS No.

000074-82-8

Methane

No definition

000074-84-0

Ethane

No definition

000074-98-6

Propane, liquefied C3H8

No definition

000075-28-5

Propane, 2-methyl-

No definition

000078-78-4

Butane, 2-methyl

No definition

000106-97-8

Butane, pure C4H10

No definition

000109-66-0

Pentane

No definition

000115-07-1

1-Propene

No definition

000287-92-3

Cyclopentane

No definition

000513-35-9

2-Butene, 2-methy.-

No definition

008006-14-2

Natural gas

Raw natural gas, as found in nature, or a gaseous combination of hydrocarbons having carbon numbers predominantly in the range of C1 through C4 separated from raw natural gas by the removal of natural gas condensate, natural gas liquid, and natural gas condensate/natural gas.

#### 068131-75-9

Gases (petroleum), C3-4

A complex combination of hydrocarbons produced by distillation of products from the cracking of crude oil. It consists of hydrocarbons having carbon numbers in the range of C3 through C4, predominantly of propane and propylene, and boiling in the range of approximately -51 °C to -1°C (-60°F to 30°F).

#### 068307-98-2

Tail gas (petroleum), catalytic cracked distillate and catalytic cracked naphtha fractionation absorber.

The complex combination of hydrocarbons from the distillation of the products from catalytic cracked distillates and catalytic cracked naphtha. It consists predominantly of hydrocarbons having carbon numbers in the range of C1 through C4.

## 068307-99-3

Tail gas (petroleum), catalytic polymn. naphtha fractionation stabilizer

A complex combination of hydrocarbons from the fractionation stabilization products from polymerization of naphtha. It consists predominantly of hydrocarbons having carbon numbers in the range of C1 through C4.

## 068308-02-1

Tail gas (petroleum), distn., hydrogen sulfide-free

No definition

## 068308-03-2

Tail gas (petroleum), gas oil catalytic cracking absorber

A complex combination of hydrocarbons obtained from the distillation of products from the catalytic cracking of gas oil. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068308-04-3

Tail gas (petroleum), gas recovery plant

A complex combination of hydrocarbons from the distillation of products from miscellaneous hydrocarbon streams. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068308-05-4

Tail gas (petroleum), gas recovery plant deethanizer

A complex combination of hydrocarbons from the distillation of products from miscellaneous hydrocarbon streams. It consists of hydrocarbon having carbon numbers predominantly in the range of C1 through C4.

## 068308-06-5

Tail gas (petroleum), hydrodesulfurized distillate and hydrodesulfurized naphtha fractionator, acid-free

A complex combination of hydrocarbons obtained from fractionation of hydrodesulfurised naphtha and distillate hydrocarbon streams and treated to remove acidic impurities. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068308-08-7

Tail gas (petroleum), isomerized naphtha fractionation stabilizer

A complex combination of hydrocarbons obtained from the fractionation stabilization products from isomerized naphtha. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

#### 068308-09-8

Tail gas (petroleum), light straight-run naphtha stabilizer, hydrogen sulfide-free

A complex combination of hydrocarbons obtained from fractionation stabilization of light straight run naphtha and from which hydrogen sulfide has been removed by amine treatment. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068308-10-1

Tail gas (petroleum), straight run distillate hydrodesulfurizer, H2S free

A complex combination of hydrocarbons obtained from catalytic hydrodesulfurization of straight run distillates and from which hydrogen sulfide has been removed by amine treatment. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068308-11-2

Tail gas (petroleum), propane-propylene alkylation feed prep deethanizer

A complex combination of hydrocarbons obtained from the distillation of the reaction products of propane with propylene. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068308-12-3

Tail gas (petroleum), vacuum gas oil hydrodesulfurizer, hydrogen sulfide-free

A complex combination of hydrocarbons obtained from catalytic hydrodesulfurization of vacuum gas oil and from which hydrogen sulfide has been removed by amine treatment. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

#### 068308-27-0

Fuel gases, refinery

A complex combination of light gases consisting of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068409-99-4

Gases (petroleum), catalytic cracked overheads

A complex combination of hydrocarbons produced by the distillation of products from the catalytic cracking process. It consists of hydrocarbons having carbon numbers predominantly in the range of C3 through C5 and boiling in the range of approximately  $-48^{\circ}$ C to  $32^{\circ}$ C ( $-54^{\circ}$ F to  $90^{\circ}$ F).

## 068410-63-9

Natural gas, dried

A complex combination of hydrocarbons separated from natural gas. It consists of saturated aliphatic hydrocarbons having carbon numbers in the range of C1 through C4, predominantly methane and ethane.

## 068475-57-0

Alkanes, C1-2

No definition

068475-58-1

Alkanes, C2-3

No definition

068475-59-2

Alkanes, C3-4

No definition

068475-60-5

Alkanes, C4-5

No definition

068476-26-6

Fuel gases

A combination of light gases. It consists predominantly of hydrogen and/or low molecular weight hydrocarbons.

068476-27-7

Fuel gases, amine system residues

The complex residuum from the amine system for removal of hydrogen sulfide. It consists primarily of hydrogen, methane and ethane with various small amounts of nitrogen, carbon dioxide and hydrocarbons having carbon numbers predominantly in the range of C3 through C5.

068476-28-8

Fuel gases, C6-8 catalytic reformer

A complex combination of gases obtained from a catalytic reforming process using C6-8 hydrocarbon feed. It consists primarily of hydrogen and methane with various small amounts of nitrogen, carbon monoxide, carbon dioxide and hydrocarbons having carbon numbers predominantly in the range of C2 through C6.

068476-29-9

Fuel gases, crude oil distillates

A complex combination of light gases produced by distillation of crude oil and by catalytic reforming of naphtha. It consists of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C4 and boiling in the range of approximately -217°C to -12°C (-423°F to 10°F).

068476-40-4

Hydrocarbons, C3-4

No definition

068476-42-6

Hydrocarbons, C4-5

No definition

068476-44-8

Hydrocarbons, C4 and higher

No definition

068476-49-3

Hydrocarbons, C2-4, C3-rich

No definition

## 068476-54-0

Hydrocarbons, C3-5, polymn. unit feed

A complex combination of hydrocarbons collected from various processes. It consists predominantly of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C3 to C5 and boiling in the range of approximately -48.degree. C to 38.degree. C (-54.degree. F to 100.degree. F).

#### 068476-85-7

Petroleum gases, liquefied

A complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C3 through C7 and boiling in the range of approximately -40°C to 80°C (-40°F to 176°F).

#### 068476-86-8

Petroleum gases, liquefied, sweetened

A complex combination of hydrocarbons obtained by subjecting liquefied petroleum gas mix to a sweetening process to convert mercaptans or to remove acidic impurities. It consists of hydrocarbons having carbon numbers predominantly in the range of C3 through C7 and boiling in the range of approximately -40°C to 80°C (-40°F to 176°F).

## 068477-25-8

Waste gases, vent gas, C1-6

A complex combination of hydrocarbons produced by the distillation of products from the vacuum unit. It consists of saturated hydrocarbons having carbon numbers in the range of C1 through C6.

## 068477-33-8

Gases (petroleum), C3-4, isobutane-rich

A complex combination of hydrocarbons from the distillation of saturated and unsaturated hydrocarbons usually ranging in carbon numbers from C3 through C6, predominantly butane and isobutane. It consists of saturated and unsaturated hydrocarbons having carbon numbers in the range of C3 through C4, predominantly isobutane.

## 068477-42-9

Gases (petroleum), extractive, C3-5, butene-isobutylene-rich

A complex combination of hydrocarbons obtained from extractive distillation of saturated and unsaturated aliphatic hydrocarbons usually ranging in carbon numbers from C3 through C5, predominantly C4. It consists of saturated and unsaturated hydrocarbons having carbon numbers predominantly in the range of C3 through C5, predominantly butenes and isobutylene.

## 068477-69-0

Gases (petroleum), butane splitter overheads

A complex combination of hydrocarbons obtained from the distillation of the butane stream. It consists of aliphatic hydrocarbons having carbon numbers predominantly in the range of C3 through C4.

## 068477-70-3

Gases (petroleum), C2-3

A complex combination of hydrocarbons produced by the distillation of products from a

catalytic fractionation process. It contains predominantly ethane, ethylene, propane, and propylene.

## 068477-71-4

Gases (petroleum), catalytic-cracked gas oil depropanizer bottoms, C4-rich acid-free

A complex combination of hydrocarbons obtained from fractionation of catalytic cracked gas oil hydrocarbon stream and treated to remove hydrogen sulfide and other acidic components. It consists of hydrocarbons having carbon numbers in the range of C3 through C5, predominantly C4.

## 068477-72-5

Gases (petroleum), catalytic-cracked naphtha debutanizer bottoms, C3-5-rich

A complex combination of hydrocarbons obtained from the stabilization of catalytic cracked naphtha. It consists of aliphatic hydrocarbons having carbon numbers predominantly in the range of C3 through C5.

#### 068477-73-6

Gases (petroleum), catalytic cracked naphtha depropanizer overhead, C3-rich acid-free A complex combination of hydrocarbons obtained from fractionation of catalytic cracked hydrocarbons and to remove acidic impurities. It consists of hydrocarbons having carbon numbers in the range of C2 through C4, predominantly C3.

## 068477-74-7

Gases (petroleum), catalytic cracker

A complex combination of hydrocarbons produced by the distillation of the products from a catalytic cracking process. It consists predominantly of aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

## 068477-75-8

Gases (petroleum), catalytic cracker, C1-5-rich

A complex combination of hydrocarbons produced by the distillation of products from a catalytic cracking process. It consists of aliphatic hydrocarbons having carbon numbers in the range of C1 through C6, predominantly C1 through C5.

## 068477-76-9

Gases (petroleum), catalytic polymd. naphtha stabilizer overhead, C2-4-rich

A complex combination of hydrocarbons obtained from the fractionation stabilization of catalytic polymerized naphtha. It consists of aliphatic hydrocarbons having carbon numbers in the range of C2 through C6, predominantly C2 through C4.

## 068477-79-2

Gases (petroleum), catalytic reformer, C1-4-rich

A complex combination of hydrocarbons produced by distillation of products from a catalytic reforming process. It consists of hydrocarbons having carbon numbers in the range of C1 through C6, predominantly C1 through C4.

## 068477-83-8

Gases (petroleum), C3-5 olefinic-paraffinic alkylation feed

A complex combination of olefinic and paraffinic hydrocarbons having carbon numbers in the range of C3 through C5 which are used as alkylation feed. Ambient temperatures normally exceed the critical temperature of these combinations.

## 068477-85-0

Gases (petroleum), C4-rich

A complex combination of hydrocarbons produced by distillation of products from a catalytic fractionation process. It consists of aliphatic hydrocarbons having carbon numbers in the range of C3 through C5, predominantly C4.

#### 068477-86-1

Gases (petroleum), deethanizer overheads

A complex combination of hydrocarbons produced from distillation of the gas and gasoline fractions from the catalytic cracking process. It contains predominantly ethane and ethylene.

#### 068477-87-2

Gases (petroleum), deisobutanizer tower overheads

A complex combination of hydrocarbons produced by the atmospheric distillation of a butane-butylene stream. It consists of aliphatic hydrocarbons having carbon numbers predominantly in the range of C3 through C4.

## 068477-88-3

Gases (petroleum), deethanizer overheads, C3-rich

A complex combination of hydrocarbons produced by distillation of products from the propylene purification unit. It consists of aliphatic hydrocarbons having carbon numbers in the range of C1 through C3, predominantly C3.

## 068477-90-7

Gases (petroleum), depropanizer dry, propene-rich

A complex combination of hydrocarbons produced by the distillation of products from the gas and gasoline fractions of a catalytic cracking process. It consists predominantly of propylene with some ethane and propane.

## 068477-91-8

Gases (petroleum), depropanizer overheads

A complex combination of hydrocarbons produced by distillation of products from the gas and gasoline fractions of a catalytic cracking process. It consists of aliphatic hydrocarbons having carbon numbers predominantly in the range of C2 through C4.

## 068477-94-1

Gases (petroleum), gas recovery plant depropanizer overheads

A complex combination of hydrocarbons obtained by fractionation of miscellaneous hydrocarbon streams. It consists predominantly of hydrocarbons having carbon numbers in the range of C1 through C4, predominantly propane.

## 068477-95-2

Gases (petroleum), Girbatol unit feed

A complex combination of hydrocarbons that is used as the feed into the Girbatol unit to remove hydrogen sulfide. It consists of aliphatic hydrocarbons having carbon numbers predominantly in the range of C2 through C4.

## 068478-19-3

Residual oils (petroleum), propene purifn. splitter

A complex residuum from the propene purification unit. It consists of aliphatic hydrocarbons having carbon numbers predominantly in the range of C3 through C4.

#### 068478-24-0

Tail gas (petroleum), catalytic cracker, catalytic reformer and hydrodesulfurizer combined fractionater

A complex combination of hydrocarbons obtained from the fractionation of products from catalytic cracking, catalytic reforming and hydrodesulfurizing processes treated to remove acidic impurities. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068478-26-2

Tail gas (petroleum), catalytic reformed naphtha fractionation stabilizer

A complex combination of hydrocarbons obtained from the fractionation stabilization of catalytic reformed naphtha. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068478-32-0

Tail gas (petroleum), saturate gas plant mixed stream, C4-rich

A complex combination of hydrocarbons obtained from the fractionation stabilization of straight-run naphtha, distillation tail gas and catalytic reformed naphtha stabilizer tail gas. It consists of hydrocarbons having carbon numbers in the range of C3 through C6, predominantly butane and isobutane.

#### 068478-33-1

Tail gas (petroleum), saturate gas recovery plant, C1-2-rich

A complex combination of hydrocarbons obtained from fractionation of distillate tail gas, straight-run naphtha, catalytic reformed naphtha stabilizer tail gas. It consists predominantly of hydrocarbons having carbon numbers in the range of C1 through C5, predominantly methane and ethane.

## 068478-34-2

Tail gas (petroleum), vacuum residues thermal cracker

A complex combination of hydrocarbons obtained from the thermal cracking of vacuum residues. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

#### 068512-91-4

Hydrocarbons, C3-4-rich, petroleum distillate

A complex combination of hydrocarbons produced by distillation and condensation of crude oil. It consists of hydrocarbons having carbon numbers in the range of C3 through C5, predominantly C3 through C4.

#### 068513-11-1

Fuel gases, hydrotreater fractionation, scrubbed

A complex combination produced by the fractionation and scrubbing of products from various hydrotreating units. It consists of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

#### 068513-12-2

Fuel gases, saturate gas unit fractionater-absorber overheads

A complex combination produced by the fractionation and absorption of products of the saturate gas unit. It consists of hydrogen and saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068513-13-3

Fuel gases, thermal cracked catalytic cracking residue

A complex combination obtained by the thermal cracking of a catalytically cracked residuum. It consists of hydrogen and saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068513-15-5

Gases (petroleum), full-range straight-run naphtha dehexanizer off

A complex combination of hydrocarbons obtained by the fractionation of the full-range s traight-run naphtha. It consists of hydrocarbons having carbon numbers predominantly in the range of C2 through C6.

## 068513-16-6

Gases (petroleum), hydrocracking depropanizer off, hydrocarbon-rich

A complex combination of hydrocarbon produced by the distillation of products from a hydrocracking process. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C4. It may also contain small amounts of hydrogen and hydrogen sulfide.

#### 068513-17-7

Gases (petroleum), light straight-run naphtha stabilizer off

A complex combination of hydrocarbons obtained by the stabilization of light straight-run naphtha. It consists of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C2 through C6.

#### 068513-65-5

Butane, branched and linear

No definition

## 068513-66-6

Residues (petroleum), alkylation splitter, C4-rich

A complex residuum from the distillation of streams from various refinery operations. It consists of hydrocarbons having carbon numbers in the range of C4 through C5, predominantly butane and boiling in the range of approximately -11.7°C to 27.8°C (11°F to 82°F).

## 068514-31-8

Hydrocarbons, C1-4

A complex combination of hydrocarbons produced by thermal cracking and absorber operations and by distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C4 and boiling in the range of approximately  $-164^{\circ}$ C to  $-5^{\circ}$ C ( $-263^{\circ}$ F to  $31^{\circ}$ F).

## 068514-36-3

Hydrocarbons, C1-4, sweetened

A complex combination of hydrocarbons obtained by subjecting hydrocarbon gases to a sweetening process to convert mercaptans or to remove acidic impurities. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C4 and boiling in the range of approximately -164°C to -0.5°C (-263°F to 31°F).

## 068527-14-0

Gases (petroleum), methane-rich off ..C1

A complex combination separated by distillation of a gas stream containing hydrogen, carbon monoxide, carbon dioxide and hydrocarbons having carbon numbers in the range of C1 through C6 or obtained by the cracking of ethane and propane. It consists primarily of methane with various small amounts of hydrogen and nitrogen.

#### 068527-16-2

Hydrocarbons, C1-3

A complex combination of hydrocarbons having carbon numbers predominantly in the range of C1 through C3 and boiling in the range of approximately minus 164°C to -42°C (-263°F to -44°F).

## 068527-19-5

Hydrocarbons, C1-4, debutanizer fraction

No definition

## 068602-83-5

Gases (petroleum), C1-5, wet

A complex combination of hydrocarbons produced by the distillation of crude oil and/or the cracking of tower gas oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068606-24-6

Hydrocarbons, C4, butene concentrator by-product

A complex combination of hydrocarbons obtained in the production of butene concentrate. It consists of hydrocarbons having carbon numbers predominantly in the range of C3 through C5.

## 068606-25-7

Hydrocarbons, C2-4

No definition

## 068606-26-8

Hydrocarbons, C3

No definition

## 068606-27-9

Gases (petroleum), alkylation feed

A complex combination of hydrocarbons produced by the catalytic cracking of gas oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C3 through C4.

## 068606-34-8

Gases (petroleum), depropanizer bottoms fractionation off

A complex combination of hydrocarbons obtained from the fractionation of depropanizer bottoms. It consists predominantly of butane, isobutane and butadiene.

## 068783-07-3

Gases (petroleum), refinery blend

A complex combination obtained from various refinery processes. It consists of hydrogen, hydrogen sulfide and hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

#### 068783-61-9

Fuel gases, refinery, sweetened

A complex combination obtained by subjecting refinery fuel gases to a sweetening process to convert mercaptans or to remove acidic impurities. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C5 a nd boiling in the range of approximately -73.degree. C to 50.degree. C (-100.degree. F to 122.degree. F).

## 068783-62-0

Fuel gases, refinery, unsweetened

A complex combination obtained by the fractionation of naphtha and compressed hydrocarbon gas streams from various refinery processes. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C5 and boiling in the range of -73.degree. C to 65.degree. C(-100.degree. F to 150.degree. F).

## 068783-64-2

Gases (petroleum), catalytic cracking

A complex combination of hydrocarbons produced by the distillation of the products from a catalytic cracking process. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C3 through C5.

## 068783-65-3

Gases (petroleum), C2-4, sweetened

A complex combination of hydrocarbons obtained by subjecting a petroleum distillate to a sweetening process to convert mercaptans or to remove acidic impurities. It consists predominantly of saturated and unsaturated hydrocarbons having carbon numbers predominantly in the range of C2 through C4 and boiling in the range of approximately - 51°C to -34°C (-60°F to -30°F).

## 068814-47-1

Waste gases, refinery vent

A complex combination obtained from various refinery processes. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C5 and hydrogen sulfide.

## 068918-98-9

Fuel gases, refinery, hydrogen sulfide-free

A complex combination of light gases consisting of hydrocarbons having carbon numbers predominantly in the range of C1 through C3. Produced from the fractionation and subsequent scrubbing of hydrotreating units.

## 068918-99-0

Gases (petroleum), crude oil fractionation off

A complex combination of hydrocarbons produced by the fractionation of crude oil. It consists of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068919-00-6

Gas (petroleum), dehexanizer off

A complex combination of hydrocarbons obtained by the fractionation of combined naphtha streams. It consists of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

#### 068919-05-1

Gases (petroleum), light straight run gasoline fractionation stabilizer off

A complex combination of hydrocarbons obtained by the fractionation of light straight-run gasoline. It consists of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

#### 068919-06-2

Gases (petroleum), naphtha unifiner desulfurization stripper off

A complex combination of hydrocarbons produced by a naphtha unifiner desulfurization process and stripped from the naphtha product. It consists of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068919-10-8

Gases (petroleum), straight-run stabilizer off

A complex combination of hydrocarbons obtained from the fractionation of the liquid from the first tower used in the distillation of crude oil. It consists of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068919-16-4

Hydrocarbons, C3-6, catalytic alkylation by-products

The complex combination of hydrocarbons obtained by the catalytic alkylation of benzene with propylene. It consists of hydrocarbons having carbon numbers predominantly in the range of C3 through C6 and boiling in the range of approximately - 40.degree.C to 70.degree.C (-40.degree.F to 158.degree.F). This stream may contain 1to 20 vol. % of benzene.

## 068919-19-7

Gases (petroleum), fluidized catalytic cracker splitter residues

A complex combination of hydrocarbons produced by the fractionation of the charge to the C3-C4 splitter. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C3 through C4.

## 068919-20-0

Gases (petroleum), fluidized catalytic cracker splitter overheads

A complex combination of hydrocarbons produced by the fractionation of the charge to the C3-C4 splitter. It consists predominantly of C3 hydrocarbons.

## 068952-76-1

Gases (petroleum), catalytic cracked naphtha debutanizer

A complex combination of hydrocarbons obtained from fractionation of catalytic cracked naphtha. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068952-81-8

Tail gas (petroleum), thermal-cracked distillate, gas oil and naphtha absorber

A complex combination of hydrocarbons obtained from the separation of thermal-cracked distillates, naphtha and gas oil. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

#### 068952-82-9

Tail gas (petroleum), thermal cracked hydrocarbon fractionation stabilizer, petroleum

coking

A complex combination of hydrocarbons obtained from the fractionation stabilization of thermal cracked hydrocarbons from petroleum coking process. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

## 068955-28-2

Gases (petroleum), light steam-cracked, butadiene conc.

A complex combination of hydrocarbons produced by the distillation of products from a thermal cracking process. It consists of hydrocarbons having a carbon number predominantly of C4.

## 068955-34-0

Gases (petroleum), straight-run naphtha catalytic reformer stabilizer overhead

A complex combination of hydrocarbons obtained by the catalytic reforming of straight-run naphtha and the fractionation of the total effluent. It consists of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C2

## 068956-54-7

Hydrocarbons, C4-unsatd.

No definition

## 071329-37-8

Residues (petroleum), catalytic cracking depropanizer, C4-rich

A complex residuum from the stabilization of catalytic cracked naphtha hydrocarbon streams. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C3 through C5, primarily C4.

## 071808-30-5

Tail gas (petroleum), thermal cracking absorber

A complex combination of hydrocarbons obtained from the separation of thermal cracked naphtha, distillates and gas oil hydrocarbons. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## **EU Category**

## Refinery Gases (Category 35)

#### CAS No.

008006-20-0

Fuel gases. Low and medium BTU

A complex combination obtained by burning coal or coke with a restricted air or oxygen supply or by blowing air or oxygen and steam through incandescent coke. The combustibles consist primarily of carbon monoxide, carbon dioxide and hydrogen.

#### 068477-65-6

Gases (petroleum), amine system feed

The feed to the amine system for removal of hydrogen sulfide. It consists of hydrogen. Carbon monoxide, carbon dioxide, hydrogen sulfide and aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5 may also be present

## 068477-66-7

Gases (petroleum), benzene unit hydrodesulfurizer off

Off gases produced by the benzene unit. It consists primarily of hydrogen. Carbon monoxide and hydrocarbons having carbon numbers predominantly in the range of C1 through C6, including benzene, may also be present.

## 068477-67-8

Gases (petroleum), benzene unit recycle, hydrogen-rich

A complex combination of hydrocarbons obtained by recycling the gases of the benzene unit. It consists primarily of hydrogen with various small amounts of carbon monoxide and hydrocarbons having carbon numbers in the range of C1 through C6.

## 068477-68-9

Gases (petroleum), blend oil, hydrogen-nitrogen-rich

A complex combination of hydrocarbons obtained by distillation of a blend oil. It consists primarily of hydrogen and nitrogen with various small amounts of carbon monoxide, carbon dioxide, and aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068477-77-0

Gases (petroleum), catalytic reformed naphtha stripper overheads

A complex combination of hydrocarbons obtained from the stabilization of catalytic reformed naphtha. It consists of hydrogen and saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068477-80-5

Gases (petroleum), C6-8 catalytic reformer recycle

A complex combination of hydrocarbons produced by distillation of products from catalytic reforming of C6-C8 feed and recycled to conserve hydrogen. It consists primarily of hydrogen. It may also contain various small amounts of carbon monoxide, carbon dioxide, nitrogen, and hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

## 068477-81-6

Gases (petroleum), C6-8 catalytic reformer

A complex combination of hydrocarbons produced by distillation of products from catalytic reforming of C6-C8 feed. It consists of hydrocarbons having carbon numbers in

the range of C1 through C5 and hydrogen.

#### 068477-82-7

Gases (petroleum), C6-8 catalytic reformer recycle, hydrogen-rich

No definition

## 068477-92-9

Gases (petroleum), dry sour, gas-concn.-unit-off

The complex combination of dry gases from a gas concentration unit. It consists of hydrogen, hydrogen sulfide and hydrocarbons having carbon numbers predominantly in the range of C1 through C3.

## 068477-97-4

Gases (petroleum), hydrogen-rich

A complex combination separated as a gas from hydrocarbon gases by chilling. It consists primarily of hydrogen with various small amounts of carbon monoxide, nitrogen, methane, and C2 hydrocarbons.

## 068477-98-5

Gases (petroleum), hydrotreater blend oil recycle, hydrogen-nitrogen-rich

A complex combination obtained from recycled hydrotreated blend oil. It consists primarily of hydrogen and nitrogen with various small amounts of carbon monoxide, carbon dioxide and hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068478-00-2

Gases (petroleum), recycle, hydrogen-rich

A complex combination obtained from recycled reactor gases. It consists primarily of hydrogen with various small amounts of carbon monoxide, carbon dioxide, nitrogen, hydrogen sulfide, and saturated aliphatic hydrocarbons having carbon numbers in the range of C1 through C5.

## 068478-01-3

Gases (petroleum), reformer make-up, hydrogen-rich

A complex combination obtained from the reformers. It consists primarily of hydrogen with various small amounts of carbon monoxide and aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068478-02-4

Gases (petroleum), reforming hydrotreater

A complex combination obtained from the reforming hydrotreating process. It consists primarily of hydrogen, methane, and ethane with various small amounts of hydrogen sulfide and aliphatic hydrocarbons having carbon numbers predominantly in the range of C3 through C5.

## 068478-03-5

Gases (petroleum), reforming hydrotreater, hydrogen-methane-rich

A complex combination obtained from the reforming hydrotreating process. It consists primarily of hydrogen and methane with various small amounts of carbon monoxide, carbon dioxide, nitrogen and saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C2 through C5.

#### 068478-04-6

Gases (petroleum), reforming hydrotreater make-up, hydrogen-rich

A complex combination obtained from the reforming hydrotreating process. It consists primarily of hydrogen with various small amounts of carbon monoxide and aliphatichydrocarbons having carbon numbers predominantly in the range of C1 through C5.

#### 068478-05-7

Gases (petroleum), thermal cracking distn.

A complex combination produced by distillation of products from a thermal cracking process. It consists of hydrogen, hydrogen sulfide, carbon monoxide, carbon dioxide and hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

#### 068478-25-1

Tail gas (petroleum), catalytic cracker refractionation absorber

A complex combination of hydrocarbons obtained from refractionation of products from a catalytic cracking process. It consists of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C3.

#### 068478-27-3

Tail gas (petroleum), catalytic reformed naphtha separator

A complex combination of hydrocarbons obtained from the catalytic reforming of straight run naphtha. It consists of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

#### 068478-28-4

Tail gas (petroleum), catalytic reformed naphtha stabilizer

A complex combination of hydrocarbons obtained from the stabilization of catalytic reformed naphtha. It consists of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

#### 068478-29-5

Tail gas (petroleum), cracked distillate hydrotreater separator

A complex combination of hydrocarbons obtained by treating cracked distillates with hydrogen in the presence of a catalyst. It consists of hydrogen and saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

#### 068478-30-8

Tail gas (petroleum), hydrodesulfurized straight-run naphtha separator

A complex combination of hydrocarbons obtained from hydrodesulfurization of straight-run naphtha. It consists of hydrogen and saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

#### 068513-14-4

Gases (petroleum), catalytic reformed straight-run naphtha stabilizer overheads

A complex combination of hydrocarbons obtained from the catalytic reforming of straight-run naphtha followed by fractionation of the total effluent. It consists of hydrogen, methane, ethane and propane.

## 068513-18-8

Gases (petroleum), reformer effluent high-pressure flash drum off

A complex combination produced by the high-pressure flashing of the effluent from the

reforming reactor. It consists primarily of hydrogen with various small amounts of methane, ethane, and propane.

## 068513-19-9

Gases (petroleum), reformer effluent low-pressure flash drum off

A complex combination produced by low-pressure flashing of the effluent from the reforming reactor. It consists primarily of hydrogen with various small amounts of methane, ethane, and propane

## 068513-68-8

Residues (petroleum), deethanizer tower

A complex residuum from the distillation of a gas stream containing hydrogen, carbon monoxide, carbon dioxide and hydrocarbons having carbon numbers in the range of C1 through C6 or from the cracking of ethane and propane. It consists of hydrocarbons having carbon numbers in the range of C2 through C6. It may contain small amounts of benzene.

## 068527-13-9

Gases (petroleum), acid, ethanolamine scrubber

A complex mixture separated from refinery gas by scrubbing with ethanolamine. It consists primarily of hydrogen sulfide and carbon dioxide. It may also contain various small amounts of hydrogen, carbon monoxide and nitrogen.

## 068527-15-1

Gases (petroleum), oil refinery gas distn. off

A complex combination separated by distillation of a gas containing hydrogen, carbon monoxide, carbon dioxide and hydrocarbons having carbon numbers in the range of C1 through C6 or obtained by cracking ethane and propane. It consists of hydrocarbons having carbon numbers predominantly in the range of C1 through C2, hydrogen, nitrogen, and carbon monoxide.

## 068602-82-4

Gases (petroleum), benzene unit hydrotreater depentanizer overheads

A complex combination produced by treating the feed from the benzene unit with hydrogen in the presence of a catalyst followed by depentanizing. It consists primarily of hydrogen, ethane and propane with various small amounts of nitrogen, carbon monoxide, carbon dioxide and hydrocarbons having carbon numbers predominantly in the range of C1 through C6. It may contain trace amounts of benzene.

## 068602-84-6

Gases (petroleum), secondary absorber off, fluidized catalytic cracker overheads fractionator

A complex combination produced by treating the feed from the benzene unit with hydrogen in the presence of a catalyst followed by depentanizing. It consists primarily of hydrogen, ethane and propane with various small amounts of nitrogen, carbon monoxide, carbon dioxide and hydrocarbons having carbon numbers predominantly in the range of C1 through C6. It may contain trace amounts of benzene. A complex combination produced by the fractionation of the overhead products from the catalytic cracking process in the fluidized catalytic cracker. It consists of hydrogen, nitrogen, and hydrocarbons having carbon numbers predominantly in the range of C1 through C3.

## 068607-11-4

Petroleum products, refinery gases

A complex combination which consists primarily of hydrogen with various small amounts of methane, ethane, and propane.

#### 068783-05-1

Gases (petroleum), ammonia-hydrogen sulfide, water-satd.

A water-saturated gas produced by the treatment of waste process water through steam stripping. It consists of up to 30% hydrogen sulfide and up to 60% ammonia.

#### 068783-06-2

Gases (petroleum), hydrocracking low-pressure separator

A complex combination obtained by the liquid-vapor separation of the hydrocracking process reactor effluent. It consists predominantly of hydrogen and saturated hydrocarbons having carbon numbers predominantly in the range of C1 through C3.

#### 068814-67-5

Gases (petroleum), refinery

A complex combination obtained from various petroleum refining operations. It consists of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C3.

#### 068814-90-4

Gases (petroleum), platformer products separator off

A complex combination obtained from the chemical reforming of naphthenes to aromatics. It consists mainly of hydrogen and saturated hydrocarbons having carbon numbers predominantly in the range of C2 through C4.

## 068911-58-0

Gases (petroleum), hydrotreated sour kerosine depentanizer stabilizer off

The complex combination obtained from the depentanizer stabilization of hydrotreated kerosine. It consists primarily of hydrogen, methane, ethane, and propane with various small amounts of nitrogen, hydrogen sulfide, carbon monoxide and hydrocarbons having carbon numbers predominantly in the range of C4 through C5.

## 068911-59-1

Gases (petroleum), hydrotreated sour kerosine flash drum

A complex combination obtained from the flash drum of the unit treating sour kerosine with hydrogen in the presence of a catalyst. It consists primarily of hydrogen and methane with various small amounts of nitrogen, carbon monoxide, and hydrocarbons having carbon numbers predominantly in the range of C2 through C5.

## 068919-01-7

Gases (petroleum), distillate unifiner desulfurization stripper off

A complex combination stripped from the liquid product of the unifiner desulfurization process. It consists of hydrogen sulfide, methane, ethane, and propane.

## 068919-02-8

Gases (petroleum), fluidized catalytic cracker fractionation off

A complex combination produced by the fractionation of the overhead product of the fluidized catalytic cracking process. It consists of hydrogen, hydrogen sulfide, nitrogen, and hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068919-03-9

Gases (petroleum), fluidized catalytic cracker scrubbing secondary absorber off

A complex combination produced by scrubbing the overhead gas from the fluidized catalytic cracker. It consists of hydrogen, nitrogen, methane, ethane and propane.

#### 068919-04-0

Gases (petroleum), heavy distillate hydrotreater desulfurization stripper off

A complex combination stripped from the liquid product of the heavy distillate hydrotreater desulfurization process. It consists of hydrogen, hydrogen sulfide, and saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of Cl through C5.

## 068919-07-3

Gases (petroleum), platformer stabilizer off, light ends fractionation

A complex combination obtained by the fractionation of the light ends of the platinum reactors of the platformer unit. It consists of hydrogen, methane, ethane, and propane.

#### 068919-08-4

Gases (petroleum), preflash tower off, crude distn.

A complex combination produced from the first tower used in the distillation of crude oil. It consists of nitrogen and saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5

## 068919-12-0

Gases, (petroleum) unifiner stripper

A combination of hydrogen and methane obtained by fractionation of the products from the unifiner unit.

## 068952-79-4

Tail gas (petroleum), catalytic hydrodesulfurized naphtha separator

A complex combination of hydrocarbons obtained from the hydrodesulfurization of naphtha. It consists of hydrogen, methane, ethane, and propane.

## 068952-80-7

Tail gas (petroleum), straight-run naphtha hydrodesulfurizer

A complex combination obtained from the hydrodesulfurization of straight-run naphtha. It consists of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

## 068955-33-9

Gases (petroleum), sponge absorber off, fluidized catalytic cracker and gas oil desulfurizer overhead fractionation

A complex combination obtained by the fractionation of products from the fluidized catalytic cracker and gas oil desulfurizer. It consists of hydrogen and hydrocarbons having carbon numbers predominantly in the range of C1 through C4.

## 068989-88-8

Gases (petroleum), crude distn. and catalytic cracking

A complex combination produced by crude distillation and catalytic cracking processes. It consists of hydrogen, hydrogen sulfide, nitrogen, carbon monoxide and paraffinic and olefinic hydrocarbons having carbon numbers predominantly in the range of C1 through C6.

## **APPENDIX 2**

## **Analysis of Refinery Gases**

While all petroleum gases are composed of the same constituent molecules, their concentrations can vary depending on their process history and end use. **Liquefied petroleum gases** are typically sold at the consumer level and hence their composition is constrained by standards established by the American Society for Testing and Materials (ASTM). **Refinery gases**, however, are typically "intermediate streams" since they are consumed or further processed within the refinery. Their composition is not constrained by any standard specifications and can vary widely depending on the crude source and current refinery operating conditions. This section discusses the general composition of refinery gas streams.

Figure 2 shows the relative abundance of major components found in samples taken from 67 refinery gas streams over a one-year period in a large Gulf Coast refinery. Each graph portrays one component. The height of the bars represents the number of samples with that concentration of the component, and the position of the bar from right to left represents the amount of the component in the sample. It shows that, with the exception of hydrogen, very few of the individual components occur at high concentrations in the gas mixtures. It also shows that the hydrocarbons can vary over a wide concentration range, although their maximum concentration tends to decrease as the molecular weight (and boiling point) increases. This is because higher molecular weight hydrocarbons condense more easily at ambient temperature and are more likely to be recovered in liquid products.

This pattern of component occurrence is representative of that expected for gas stream compositions in typical petroleum refineries. The shapes of the histograms might be different for different refineries, but the constituents, the overall character, and the variability in constituent concentrations from sample-to-sample and stream-to-stream would be similar. If gas streams that are known to be more similar are grouped together, the patterns in these graphs change but the constituent concentrations still vary significantly. For example, Figure 3 summarizes the components found in 900 separate analyses of 11 different **fuel gas** streams (a subset of the 67 streams portrayed in Figure 2). It shows that methane occurs at higher concentrations in fuel gases and that there is little to no hydrogen sulfide or oxygen present in fuel gases. Similarly, Figure 4, which contains a subset of 25 streams considered to be **"hydrogen-rich,"** shows high concentrations of hydrogen and no nitrogen or oxygen.

It should be noted that the TSCA definitions for refinery gas streams do not typically specify concentrations of the individual hydrocarbon constituents. They only specify constituents likely to be found in significant quantities in the stream. Not shown in these graphs is that constituent concentrations for any one stream can also vary widely within the refinery, and from refinery to refinery, depending on the crude source and operating conditions. For these reasons, it is possible for a particular gas stream to reasonably match the description of numerous CAS numbered streams listed on the TSCA inventory. More important is the recognition that the gas streams covered in this test are all comprised of the same basic hydrocarbon components and vary only in their relative abundance and occurrence of inorganic constituents.

## **Detailed Description of Figures 2 to 4**

Figures 2 to 4 show frequency histograms for 18 major constituents of 67 different refinery gases. The constituent name is in the upper right corner of each histogram. Its concentration in mole% (molecules of constituent per 100 molecules of total sample) is shown on the X-axis. The height of each bar represents the number of analyses with similar constituent concentrations. Each histogram is scaled independently, so the concentrations displayed on the X-axis are different for each histogram and constituent.

The hydrocarbons start with **hydrogen** in the upper left of the figure and move down and then right across the page with increasing molecular weight ending with **naphtha** at the top of the 3<sup>rd</sup> column. Significant inorganic constituents appear below naphtha in the 3<sup>rd</sup> column. If a constituent is not detected in any sample included on the figure, then the histogram for that constituent is left blank. For example, hydrogen sulfide was not detected in significant quantities by the analytical method used for any of the fuel gas samples in Figure 3.

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The constituent concentrations in Figures 2 to 4 were measured using various gas chromatography methods depending on the nature and composition of the stream being analyzed. The methods used are well known and in common use within the industry. While the analytical methods used are appropriate for measuring major constituents, they are not sensitive enough to detect trace constituents in the parts-per-million concentration range.

Some constituents are combined and shown on a single histogram either for simplicity or due to limitations in the analytical methods used. Histograms labeled "butenes" display the total concentration of all olefin constituents with 4 carbons listed in Table 2 (1-butene, cis-2-butene, trans-2-butene, 2-methylpropene, and 1,2-butadiene and 1,3-butadiene if present). Histograms labeled "pentenes" similarly display the total concentration of all olefin constituents with 5 carbons in Table 2.

The histograms labeled "Naphtha" located in the upper right of Figures 2 to 4 are examples of the carbon number overlap between the test plan categories. This is discussed in the section "Description of the Petroleum Gases Category." (Note: Naphtha as used here describes an intermediate used to make the finished product Gasoline). This histogram contains the concentration of residual Naphtha that was not removed from the gas stream during processing. Due to the nature of petroleum and the separation methods used in petroleum refining, small concentrations of hydrocarbons heavier, lighter, or both than the hydrocarbons primarily addressed in each test plan will always be present. The composition of the hydrocarbons shown in the "Naphtha" histogram are similar to the intermediate streams covered in the forthcoming Gasoline Test Plan and will be addressed there. The material in the "Naphtha" histogram is in effect Gasoline that was not removed from the gas stream during processing.

Figure 2 All Gas Streams in a Sample Refinery (Based on 5950 Analyses of 67 Streams)

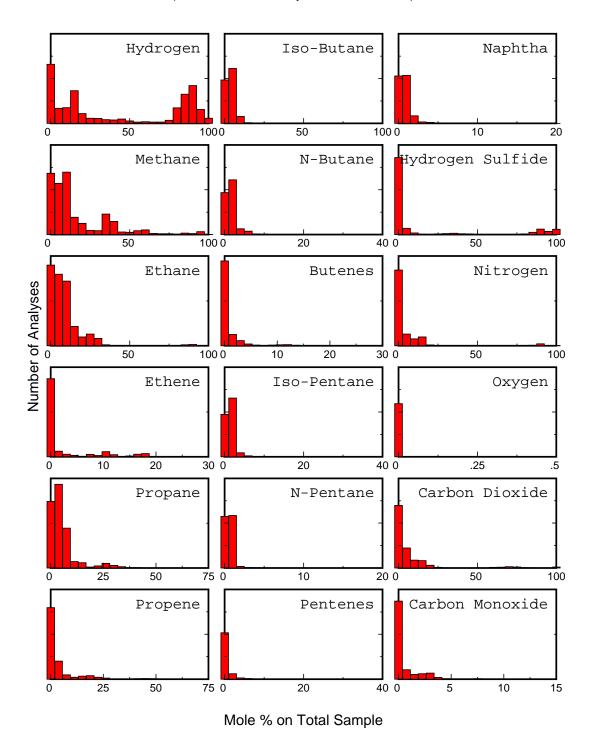


Figure 3
Fuel Gas Streams in a Sample Refinery (Based on 900 Analyses of 11 Streams)

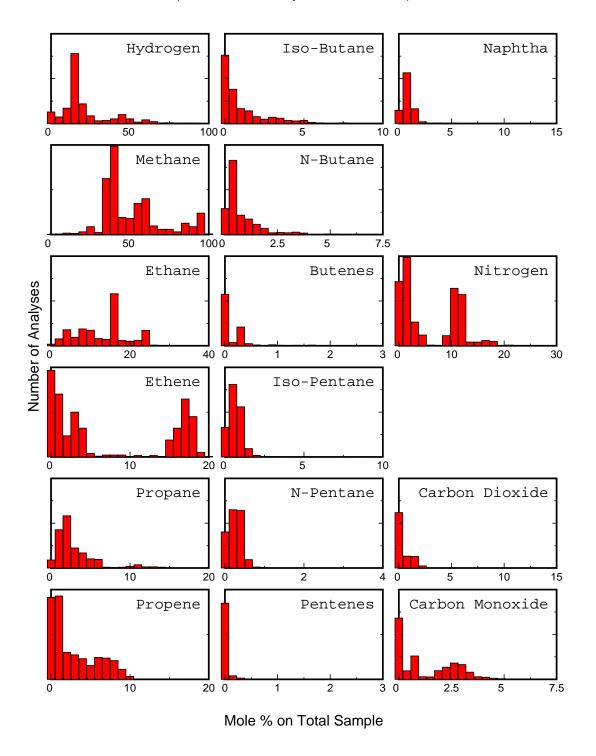
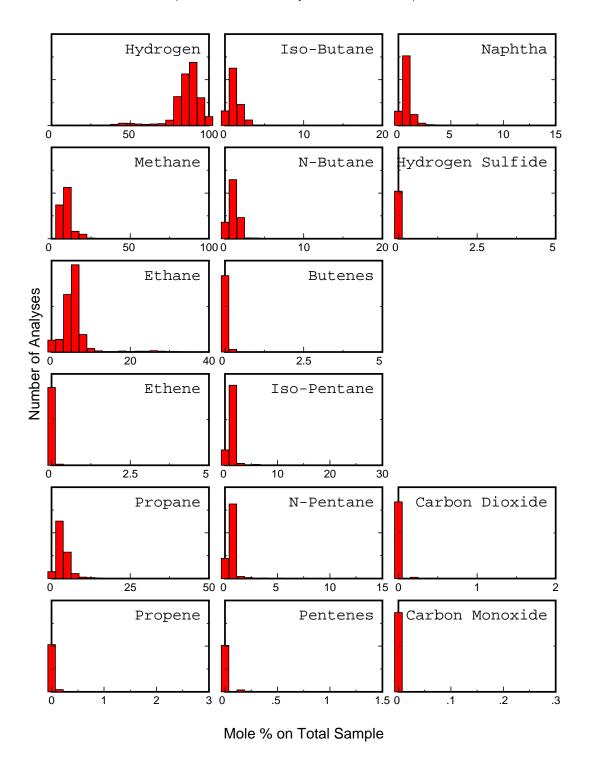


Figure 4 Hydrogen Rich Gases in a Refinery (Based on 2170 Analyses of 25 Streams)



## **APPENDIX 3**

## **Robust Summaries for Petroleum Gases**

Consortium Registration # 110997

Explanatory Note for Robust Summary Format

The Petroleum HPV Testing Group has elected to use the IUCLID (International Uniform Chemical Information Database) database as the repository for robust summaries for this program. IUCLID has been structured to accommodate a wide variety of data so that it can be used as a repository for all available data on any given chemical or category of chemicals. Many of the data elements (e.g. OECD company location and production information, packaging information, emergency procedures, etc.) are outside the SIDS (Screening Information Data Set) requirements of the US HPV Chemical Challenge. Consequently, only those fields relevant to existing data and proposed testing in support of the Petroleum Gases Test Plan are presented in this document.

# ROBUST SUMMARY OF INFORMATION ON

## Substance Group PETROLEUM GASES

Summary prepared by American Petroleum Institute

Creation date 2 NOVEMBER 1999

Printing date: 15 AUGUST 2000

Date of Last Update: 15 AUGUST 2000

NB. Reliabiliy of data included in this summary has been assessed using the approach described by Klimisch et al.

Klimisch, H. J., Andreae, M. and Tillman, U, (1997)

A systematic approach for evaluating the quality of experimental toxicological and ecotoxicological data.

Regulatory Toxicology and Pharmacology 25, 1-5.

## 1.1 GENERAL SUBSTANCE INFORMATION

Substance type: Petroleum product

Physical status: Gaseous

Petroleum gases are obtained from natural gas processing and petroleum refining operations. They are typically Class II substances on the TSCA Inventory which are "Chemical Substances of Unknown or Variable Composition, Complex Reaction Products, and Biological Materials." Their

Composition, Complex Reaction Products, and Biological Materials." Their toxicity may be assessed from a consideration of the toxicity of the individual

components.

This summary includes the available information on the following

components:

Methane Ethane Propane normal Butane iso Butane

Where available, physico-chemical data are also included for normal and iso-

pentane.

For information on published reviews of information available on other individual hydrocarbons, which may be components of petroleum gas, see

Section 1.17.

#### 1.2 SYNONYMS

Petroleum gas

Liquefied petroleum gas

LPG

#### 1. General information

#### 1.8 OCCUPATIONAL EXPOSURE LIMIT VALUES

Type of limit: TLV (US)

Limit value: 1000 ppm for LPG

Schedule: 8 hour(s)

Remark: In addition to the TLV established for LPG by the ACGIH, they have also

established TLVs for the following hydrocarbons that are likely to be present

in petroleum gas:

Methane No TLV listed as a simple asphyxiant
Ethane No TLV listed as a simple asphyxiant
Propane 2500 ppm critical effect simple asphyxiant

Butane 800 ppm critical effect narcosis

Pentane (all isomers) 600 ppm critical effects irritation and narcosis.

(1)

## **1.17 REVIEWS**

Reviews have been prepared on n-Pentane and 1,3-butadiene.

In addition a review of the available toxicological information on 9 individual hydrocarbons has also been published.

(7, 9, 19, 20)

## 2.1 MELTING POINT

**Value:** -189.7 to -130° C

Decomposition:noSublimation:noGLP:no data

Remark: Values given above span the range for the hydrocarbons that may be present

in Petroleum gas. Values for the individual hydrocarbons are as follows:

Methane -182°C
Ethane -183.3°C
Propane -189.7°C
n-Butane -138.4°C
iso-Butane -159.4°C
n-Pentane -130°C
iso-Pentane -159°C

Reliability: 1, valid without restriction. Data are taken from the CRC Handbook of

chemistry and physics

(8)

#### 2.2 BOILING POINT

**Value:** -164 to -0.5° C at 1013 hPa

**Decomposition:** no **GLP:** no data

**Remark:** Values given above span the range for the hydrocarbons that may be present

in Petroleum gas. Values for the individual hydrocarbons are as follows:

Methane -164°C
Ethane -88.6°C
Propane -42.1°C
n-Butane -0.5°C
iso-Butane -11.7°C
n-Pentane -36.1°C
iso-Pentane -27.8°C

Reliability: 1, valid without restriction. Data are taken from the CRC Handbook of

chemistry and physics.

(8)

## 2.3 DENSITY

Type: Relative density
Value: 0.3 to 0.584
GLP: no data

**Remark:** Relative densities given above span the range of values for the hydrocarbons

(liquid) that may be present in Petroleum gas. Relative densities (15/15°C) of

the individual liquid hydrocarbons are:

 Methane
 0.3 (estimated)

 Ethane
 0.35619

 Propane
 0.50698

 n-Butane
 0.58402

 iso-Butane
 0.56286

 n-Pentane
 0.63108

**Reliability:** 4, not assignable

(11)

#### 2. Physico-chemical data

#### 2.4 VAPOUR PRESSURE

Value: 1147 to 350000 hPa

GLP: no data

Remark: Values given above span the range of values for the individual hydrocarbons

that may be present in Petroleum gas. Values for the individual hydrocarbons

are shown below.

The units are given as hPa (abs) @313.15K

Methane 350000 (estimated) Ethane 60000 (estimated)

Propane 13698 n-Butane 3796.1 iso-Butane 5308.9 n-Pentane 1147 iso-Pentane 1513.1

Reliability: 4, not assignable

(11)

#### 2.5 PARTITION COEFFICIENT

log Pow: $\leq 2.3$ Year:1993GLP:no data

Remark: Measured values have been taken from the Pomona College Log Pow Data

Base

Log Pow values for the individual hydrocarbons that may be present in

Petroleum gas are:

Propane 2.3 n-Butane 2.8 iso-Butane 2.8

**Reliability:** 4, not assignable. Data taken from an on-line database.

(17)

#### 2.6.1 Water Solubility

No data

#### 2. Physico-chemical data

#### 2.7 Flash Point

**Value:** Approx. –60° C

GLP: no data

Remark: Flash points for the individual hydrocarbons that may be present in

Petroleum gas are as follows:

Hydrocarbon Flash Point (°C)

Methane -187.78
Ethane -135
Propane -104.44
n-Butane -60
iso-Butane -82.7

**Reliability:** 4, not assignable

(23)

#### 2.8 AUTO FLAMMABILITY

Value: 410 to 540° C GLP: no data

Remark: Autoignition temperatures for the individual hydrocarbons that may be

present in Petroleum gas are as follows:

Hydrocarbon	Autoignition Temperature (°C)
Methane	540
Ethane	515
Propane	450
n-Butane	405
iso-Butane	462

Reliability: 4, not assignable

(16)

## 2.9 FLAMMABILITY

Extremely flammable

#### 2.10 EXPLOSIVE PROPERTIES

Remark: UELs and LELs for the individual hydrocarbons that may be present in

Petroleum gas are as follows:

	LEL (%vol)	UEL (%vol.)	
Methane	5.0	15	
Ethane	3.0	12.5	
Propane	2.12	9.35	
n-Butane	1.86	8.41	
iso_Butane	1.8	8.44	
n-Pentane	1.4	7.8	
iso-Pentane	1.32	-	

Reliability: 1, valid without restriction. Data are taken from the CRC Handbook of

chemistry and physics.

(8)

#### 3. Environmental Fate and Pathways

## 3.1.1 Photodegradation

Type: Air Light source: Sun light

**INDIRECT PHOTOLYSIS** 

Sensitizer: OH

Conc. of sens.: 1000000 molecule/cm<sup>3</sup>

Method: Calculated according to Atkinson 1990

GLP:

**Test substance:** Methane, ethane, propane, n-butane and iso-butane.

Result: Atkinson gives rate constants which enable half lives to be calculated for

degradation of hydrocarbons in contact with hydroxyl radicals in the troposphere, under the influence of sunlight. The calculated half lives for the

components of petroleum gas are as follows:

ConstituentHalf Life (Days)Methane960Ethane30Propane7Isobutane3.4n-butane3.2

**Reliability:** 4, not assignable. Calculations were made using the constants listed in

reference by Atkinson.

(4)

## 3.1.2 Stability in Water

Not applicable

## 3.1.3 Stability in Soil

Not applicable

## 3.2 MONITORING DATA (ENVIRONMENT)

#### 3.3.1 Transport between Environmental Compartments

**Type:** volatility

**Remark:** In the event of an accidental release of any of the C<sub>1</sub> to C<sub>4</sub> hydrocarbons to

the environment, all of the material will end up in the air compartment due to

the volatility of the hydrocarbons.

#### 3. Environmental Fate and Pathways

#### 3.3.2 Distribution

Media:air - biota - sediment(s) - soil - waterMethod:Calculation according Mackay, Level I

Method: Distribution has been calculated according to Mackay Level 1. using

parameters defined by van der Zandt and van Leeuwen.

**Result:** Results for the  $C_1$  to  $C_4$  hydrocarbons are as follows:

$C_1$ to $C_4$	Air	Water	Soil	Sediment	Suspended	Biota
<u>Hydrocarbons</u>	(%)	(%)	(%)	(%)	matter (%)	(%)
•	100	0	0	0	0	0

(18, 27)

#### 3.4 MODE OF DEGRADATION IN ACTUAL USE

Petroleum gases used as fuels are burnt to yield mainly carbon dioxide, carbon monoxide and water vapour. When the unburned hydrocarbons enter the atmosphere they are photodegraded by reaction with hydroxyl radicals.

See section 3.1.1.

(3)

#### 3.5 BIODEGRADATION

Type: aerobic

Inoculum:adapted microorganismsDegradation:76.2 % after 35 dayResult:inherently biodegradable

Year: 1963
GLP: no data
Test substance: Methane

Method: The 35 day BOD was determined at 25°C using 1.0 mg of methane and

mixed cultures of hydrocarbon oxidising bacteria. The hydrocarbon was dispersed in the BOD solution by adsorption on ignited sand. No further

details of the test method are provided.

**Reliability** 4, not assignable. Insufficient information given in the publication.

(30)

Type: aerobic

Inoculum:adapted microorganismsDegradation:65.7 % after 35 dayResult:inherently biodegradable

Year: 1963
GLP: no data
Test substance: Ethane

**Method:** The 35 day BOD was determined at 25°C using 1.0 mg of ethane and mixed

cultures of hydrocarbon oxidising bacteria. The hydrocarbon was dispersed in the BOD solution by adsorption on ignited sand. No further details of the

test method are provided.

**Reliability:** 4, not assignable. Insufficient information given in the publication.

(30)

#### 3.8 ADDITIONAL REMARKS

The ability of bacteria to use  $C_1$  to  $C_4$  hydrocarbons as a carbon source has been demonstrated in a number of studies.

Fuerst & Stephens demonstrated that *Methylococcus* and other cultures were able to use methane as a carbon source. Also, organisms such as *Neurospora crassa* were able to grow utilizing ethane. Stephens et al. have also shown that butane supports the growth of *N. crassa*.

O'Brien & Brown showed that both butane and iso-butane support growth of *Mycobacterium phlei* and also that butane supports the growth of *Mycobacterium crassa*.

Vestal and Perry found that ethane, propane and butane promoted the growth of *Mycobacterium vaccae*, suggesting that these hydrocarbons are biodegradable.

In contrast, studies by Wanatabe & Takesue and by Rode & Foster have shown that butane is also able to inhibit the growth of certain bacteria, moulds, fungi and plant seeds.

(10, 21, 22, 25, 28, 29)

4. Ecotoxicity

## **AQUATIC ORGANISMS**

#### 4.1 ACUTE/PROLONGED TOXICITY TO FISH

 Exposure period:
 96 hour(s)

 Unit:
 mg/l

 TLM96:
 > 1000

 GLP:
 no data

**Test substance:** Methane, propane and butane

**Remark:** The value is cited in Patty, but it has not been possible to obtain the original

reference. The basis for this value, therefore, is not clear. Furthermore, it is now considered that aquatic toxicity of petroleum gases is not applicable.

**Reliability:** 4, not assignable. This information is not reliable.

(23)

#### **4.2 ACUTE TOXICITY TO AQUATIC INVERTEBRATES**

Not applicable

## 4.3 TOXICITY TO AQUATIC PLANTS E.G. ALGAE

Not applicable

## 4.4 TOXICITY TO MICROORGANISMS E.G. BACTERIA

See section 5.5 below

## 4.5 CHRONIC TOXICITY TO AQUATIC ORGANISMS

Not applicable

#### **5.1 ACUTE TOXICITY**

#### 5.1.1 Acute Oral Toxicity

Not applicable

#### 5.1.2 Acute Inhalation Toxicity

Type:  $LC_{50}$  Species: rat

Sex: male/female

Number of Animals: 6

**Vehicle** substance administered with air

**Exposure time:** 15 minute(s)

**Value:**  $> 800000 \text{ ppm } [= 1,442,847 \text{ mg/m}^3]$ 

Year: 1982 GLP: no data

**Test substance:** Propane, purity not specified

**Test condition:** Propane was passed through a calibrated rotameter and mixed with the

required amount of air. As soon as the concentration of propane exceeded 25%, oxygen was mixed with the air to maintain an oxygen concentration of

20%.

**Method:** Groups of either 6 male or 6 female rats were exposed for 15 minutes in 500-

ml whole body inhalation chambers. The animals were observed for effects on the CNS over a 10-minute exposure period. The EC $_{50}$  CNS effect concentration (10-min) was calculated. The concentrations causing death after 15 minutes exposure were recorded and the LC $_{50}$  (15-min) was calculated. A range of concentrations was used such that the no effect concentration, the 100% effect concentration and several in-between concentrations were determined. [Details of actual concentrations are not

provided].

**Result:** Propane caused CNS depression. Signs of intoxication were slight ataxia,

loss of righting reflex, loss of movement, narcosis, shallow respiration and death eventually from respiratory depression. Recovery from a non-lethal exposure was rapid and the rats appeared normal within 10 minutes. Where

death occurred, it was during exposure, never afterwards.

The calculated EC<sub>50</sub> and LC<sub>50</sub> values with 95% confidence limits, expressed

as concentrations in air are as follows:

EC<sub>50</sub> (CNS depression, 10 min.) 280000 (220000-350000) ppm

 $[ = 504,996 (396,783-631,245) \text{ mg/m}^3 ]$ 

 $LC_{50}$  (15 min.) >800000 ppm [= 1,442,847 mg/m<sup>3</sup>]

Reliability: 2, valid with restrictions. Study not performed to guidelines and some

experimental details lacking.

(6)

Type:  $LC_{50}$  Species: rat

Sex: male/female

Number of Animals: 6

Vehicle: substance administered with air

**Exposure time:** 15 minute(s)

**Value:**  $570000 \text{ ppm } [= 1,355,015 \text{ mg/m}^3]$ 

Year: 1982 GLP: no data

**Test substance:** Isobutane, purity not specified

Test condition: Isobutane was passed through a calibrated rotameter and mixed with the

required amount of air. As soon as the concentration of isobutane exceeded 25%, oxygen was mixed with the air to maintain an oxygen concentration of

20%.

**Method:** Groups of either 6 male or 6 female rats were exposed for 15 minutes in 500-

ml whole body inhalation chambers. The animals were observed for effects on the CNS over a 10-minute exposure period. The EC $_{50}$  CNS effect concentration (10-min) was calculated. The concentrations causing death after 15 minutes exposure were recorded and the LC $_{50}$  (15-min) was calculated. A range of concentrations was used such that the no effect concentration, the 100% effect concentration and several in-between concentrations were determined. [Details of actual concentrations are not

provided].

Result: Isobutane caused CNS stimulation. Signs of intoxication were slight tremors

of the limbs, marked tremors of the limbs and head, convulsions, narcosis, shallow respiration and death from respiratory depression. Recovery from a non-lethal exposure was rapid and the rats appeared normal within 10 minutes. Where death occurred, it was during exposure, never afterwards. The calculated  $EC_{50}$  and  $LC_{50}$  values with 95% confidence limits, expressed

as concentrations in air are as follows:

EC<sub>50</sub> (CNS stimulation, 10 min.) 200000 (160000-230000) ppm

 $[= 475,444 (380,355-546,760) \text{ mg/m}^3]$ 

LC<sub>50</sub> (15 min.) 570000 (480000-650000) ppm

 $[= 1,355,015 (1,141,065-1,545,192) \text{ mg/m}^3]$ 

Reliability: 2, valid with restrictions. Study not performed to guidelines and some

experimental details lacking.

(6)

 $\begin{tabular}{lll} \textbf{Type:} & $LC_{50}$ \\ \textbf{Species:} & $rat$ \\ \textbf{Sex:} & $no\ data$ \\ \textbf{Exposure time:} & $4\ hour(s)$ \\ \end{tabular}$ 

**Value:**  $658 \text{ mg/l} \ [\equiv 658 \text{g/m}^3]$ 

Year: 1969 GLP: no data

**Test substance:** Butane, no further specification

Method: Method not described, dose levels, group sizes, observation period not

specified. LC<sub>50</sub> stated to be estimated by Litchfield & Wilcoxon method.

Result: Study was conducted to determine butane levels in several organs. Butane

was found in brain, kidney, liver and perinephric adipose tissue.

Reliability: 3, invalid. Study not performed to guidelines and some experimental details

lacking.

(24)

Type: $LC_{50}$ Species:mouseSex:no dataExposure time:2 hour(s)

**Value:**  $680 \text{ mg/l} \ [\equiv 680 \text{ g/m}^3]$ 

Year: 1969 GLP: no data

**Test substance:** Butane, not specified further

**Method:** No details given of experimental conditions.

Result: Confidence limits given as 596-775. LC<sub>50</sub> value and limits determined by

method of Litchfield & Wilcoxon.

**Reliability:** 3, invalid. Study not performed to guidelines and some experimental details

lacking.

(24)

**Exposure time:** 5 minute(s) **Year:** 1982 **GLP:** no data

**Test substance:** Propane and isobutane

**Method:** Method not described, but reference given to previous publication by authors

which does include a description of the method.

**Result:** EC<sub>50</sub> for cardiac sensitization to adrenaline in dogs after 5 mins. exposure to

propane and isobutane are given below. Values given are the EC<sub>50</sub>

expressed as concentration in air (ppm) with 95% confidence limits.

Propane 180000 (120000-260000)

[Equivalent to 324,640 (216,427-468,925) mg/m<sup>3</sup>]

Isobutane 70000 (47000-106000)

[Equivalent to 166,405 (111,729-251,985) mg/m<sup>3</sup>]

**Reliability:** 4, not assignable. Inadequate description of study.

(6)

**Type:** cardiac sensitization to epinephrine

Species: dog Vehicle: air

Exposure time: 10 minute(s)
Year: 1948
GLP: no data

**Test substance:** Ethane, propane, n-Butane, iso-Butane

**Method:** Electrocardiograms, Lead II, were recorded from the unanaesthetised dogs.

Epinephrine hydrochloride solution (1:100000) was injected i.v. at a dose of 0.01 mg/Kg over a 25 to 40 second time interval. After administration of the epinephrine HCl another ECG was taken. Each animal was subsequently permitted to breathe a mixture of hydrocarbons in varying concentrations (15 to 90%) mixed with oxygen. After 10 minutes' inhalation of the hydrocarbon an ECG trace was made following administration of epinephrine HCl as

described above.

**Result:** Sensitisation of the myocardium occurred at the following incidence:

Hydrocarbon No. of dogs sensitised/No. exposed

Ethane 2/4
Propane 3/3
n-Butane 2/2
iso-Butane 2/2

The authors reported the results with 12 different hydrocarbons. Only those

of relevance to this dossier are summarised here.

Remark: This work is an experimental study carried out as part of a programme to

examine the usefulness of different materials as anaesthetics. Although not a guideline study, it nevertheless demonstrates the potential of some

hydrocarbons to sensitise the myocardium to epinephrine.

**Reliability:** 4, not assignable

(15)

## 5.1.3 Acute Dermal Toxicity

Not applicable

#### 5.1.4 Acute Toxicity, other Routes

Not applicable

#### 5.2 CORROSIVENESS AND IRRITATION

#### 5.2.1 Skin Irritation

Not applicable. However, evaporation of liquefied petroleum gas from the skin will cause cold burns.

15/23

## 5.2.2 Eye Irritation

Species:rabbitConcentration:undilutedTest substance:Butane

Remark: The following statement is made in Grant's Toxicology of the Eye, under the

heading Butane:

"Butane is an essentially non-toxic petroleum gas which causes no disturbance of the eye, even when injected into the anterior chamber experimentally in rabbits. I found it disappeared spontaneously from the eye

in two to four days, causing no disturbance."

No other details are provided.

Reliability: 3, invalid. This is an unreliable piece of anecdotal information and should not

be used in an evaluation of the eye irritancy potential of butane.

(12)

## **5.3 SENSITIZATION**

Not applicable

#### **5.4 REPEATED DOSE TOXICITY**

Species: rat

Sex:male/femaleStrain:Fischer 344Route of administration:inhalationExposure period:90 days

Frequency of treatment: 6 hours/day, 5 days/week

Post. observation. period: None

**Doses:** 0, 1017 & 4489 ppm  $[= 0, 2709 \& 11,959 \text{ mg/m}^3]$ 

**Control Group:** yes, concurrent no treatment

NOAEL: 4489 ppm

Method: OECD Guide-line 413 "Subchronic Inhalation Toxicity: 90-day Study"

Year: 1986 GLP: no data

**Test substance:** Two mixtures were tested as follows:

n-butane/n-pentane 50/50 wt.% isobutane/isopentane 50/50 wt.%

The mixtures were prepared by gravimetrically filling gas cylinders with 50lb. of each component and then compressing the cylinders to 250 psi. The

components were 99% minimum purity.

**Test condition:** Inhalation exposures were conducted in Rochester-type 1m<sup>3</sup> stainless steel

chambers. Test atmospheres were achieved by flash evaporation of the liquid phase components as they were released from the storage cylinders. Hydrocarbon concentrations in the chambers were monitored and adjustments made as necessary in order to achieve the desired

atmospheres.

Method: 20 male and 10 female six-week-old rats were exposed to each

concentration, 6 hours each day for 5 days each week. Total duration of the study was 90 days. A negative control group of 40 male and 20 female rats were exposed to filtered air under otherwise similar conditions. The rats were observed daily throughout the study, were weighed weekly and immediately prior to sacrifice. Necropsies were performed on half the male rats in each treatment group after the 20th exposure and for the remaining animals at the conclusion of the 90-day study. At necropsy, the presence of lesions and other abnormal conditions was noted and liver and kidney weights determined. Major tissues, except for kidneys were collected and fixed, but not examined microscopically. Kidneys were fixed and examined

histologically.

**Result:** There were no mortalities in the study.

Possible treatment-related but NOT dose-related effects included transient hunched posture and/or lethargy and intermittent tremor. Statistically significant decreases in body weight occurred in both sexes by weeks 3 and 4 when exposed to the n-butane/n-pentane mixture. Recovery occurred by

the end of the study for males but not for the females.

There were no treatment-related gross lesions observed, nor were there any

kidney or liver weight changes following exposure.

Nephrotoxicity was observed after 20 exposures in males at both dose groups of the butane/pentane mixture but this had disappeared by 90 days. A similar effect was seen in males after 20 exposures to 1000 ppm of the isobutane/isopentane mixture, but again this was not apparent in the rats exposed for 90 days. The authors concluded that although there had been a

slight nephrotoxic response in male rats after 20 exposures, this was

transient and was not present after 90 days exposure.

It is concluded, therefore that the NOAEL (concentration) is 4489 ppm.

**Reliability:** 1, valid without restriction

Remark: The purpose of this study was to examine the possible nephrotoxic effects of

 $C_4$  and  $C_5$  hydrocarbons present in gasoline. Due to the limited scope of the study, organ weight measurements were restricted to kidney and liver and

histopathological examinations also restricted to the kidney.

(2)

#### **5.5 GENETIC TOXICITY 'IN VITRO'**

Type: Ames test

**System of testing:** Salmonella typhimurium, reverse mutation assay using strains TA98, TA100,

TA1535, TA1537 & TA1538.

**Concentration:** Concentrations ranging between 1 to 50% in air.

Metabolic activation: with and without

Result: negative

**Method:** OECD 471, modified to test gaseous substances

Year: 1980 GLP: no data

**Test substance:** Gases of the following 6 compositions were tested:

n-Butane 99.7% iso-Butane 0.3%

 iso-Butane
 96.3%

 n-Butane
 3.8%

 Propane
 0.3%

 Propane
 >99.9%

 iso-Butane
 trace

 n-Butane
 trace

iso-Pentane 97.2% n-Pentane 2.8%

n-Pentane 98.7% cycloPentane 0.6% cis-Pentane-2 -

iso-Butane 97.4%

n-Butane 2.19% Propane 0.4% Ethane 0.01%

Method:

Duplicate plates seeded with the respective Salmonella strains (with and without S9 fractions) were placed in desiccators from which air was withdrawn and replaced by the gases under test. Test concentrations were 10, 20, 30, 40 and 50% in air.

The plates were exposed for 6 hours to the gas mixtures in the sealed desiccators, after which time they were removed and incubated at 37°C for an additional 40-45 hours. The number of histidine revertants were counted and recorded. Negative and positive (methylene chloride) controls were also carried out. Rat S9 fractions were used for metabolic activation.

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Result:

5. Toxicity

The positive control (methylene chloride) was mutagenic in strains TA98 and TA100 and was slightly mutagenic in TA1535.

Neither n-butane, iso-butane nor propane were toxic or mutagenic at any of the concentrations tested.

Iso pentane was toxic at concentrations of 10% and above. Further studies were carried out at 1, 2, 5 and 8% and no mutagenicity was found at these lower concentrations.

n-Pentane was toxic at concentrations of 25 and 50%. Further studies were carried out at 1, 2, 5, 8 and 10% and no mutagenicity was found at these non-toxic concentrations.

Iso butane was weakly toxic at a concentration of 50% but was not mutagenic at concentrations of 5, 10, 20, 30 or 40%.

In conclusion, none of the hydrocarbons were mutagenic with or without metabolic activation in the Ames Salmonella assay in 5 strains exposed for 6 hours in desiccators.

Reliability: 1, valid without restriction

(14)

#### **5.6 GENETIC TOXICITY 'IN VIVO'**

No data

#### **5.7 CARCINOGENICITY**

No data

#### **5.8 TOXICITY TO REPRODUCTION**

No data

## 5.9 DEVELOPMENTAL TOXICITY/TERATOGENICITY

No data

#### 5.11 EXPERIENCE WITH HUMAN EXPOSURE

During laboratory investigations of workers bottling liquefied propane and butane, most of the workers complained of respiratory symptoms, e.g. dry cough and dry throat together with gastrointestinal effects. The electrocardiographic findings in some workers indicated sinus tachycardia, extrasystole and incomplete right bundle branch block.

(5)

Lactic acid production in workers experiencing propane "poisoning" has been reported as slight.

(5)

Eight adult volunteers of both sexes were exposed to isobutane in a controlled-environment chamber to monitor their physiological responses to a series of gas concentrations ranging from 250 to 1000 ppm [ $\equiv$  594-2377mg/m<sup>3</sup>].

Initially, the response to exposure periods of 1 and 2 minutes, and 1, 2 and 8 hours were studied. Since there were no untoward responses, the eight volunteers were then exposed repetitively to isobutane at a concentration of 500 ppm [ $\equiv$  1189 mg/m<sup>3</sup>] for 1, 2 or 8 hours a day, five days a week for 2 weeks. This was followed by studying the effects of exposure to 2 mixtures of isobutane and propane for 1, 2 or 8 hours a day for 2 days. During the studies, the subjects were kept under strict medical surveillance. No untoward subjective or physiological responses were recorded either during or after the exposures. Special attention was placed on evaluating cardiac and respiratory effects by the use of continual ECG telemetry and computerised spirometric measurements. Additionally, the following serial laboratory investigations were unaltered by the exposures: complete blood count, urinalysis, serum alkaline phosphatase, SGOT, LDH, serum bilirubin, blood sugar, serum calcium, serum phosphorus, BUN, spontaneous EEG, visual evoked responses, a battery of cognitive tests and an ACTH stimulation test.

(26)

Ikoma records 20 cases of sudden death in which propane and propylene were found in the blood, urine and cerebrospinal fluids of the victims.

(13)

- 1. ACGIH (1998) Threshold limit values and Biological exposure indices for 1998-90. Cincinnatti, Ohio: American Conference of Governmental Industrial Hygienists.
- 2. Aranyi, C., O'Shea, W.J., Halder, C.A., Holdsworth, C.E. and Cockrell, B.Y. (1986).

Absence of hydrocarbon-induced nephropathy in rats exposed subchronically to volatile hydrocarbon mixtures pertinent to gasoline.

Toxicology and Industrial Health, vol. 2 No. 1, pp 85-98

3. Atkinson, R. (1985)

Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions.

Che. Rev. Volume 85, pp 69-201

4. Atkinson, R. (1990)

Gas-phase tropospheric chemistry of organic compounds: a review.

Atmospheric Environment Vol. 24A, pp 1-41

5. Aviado, D.M., Zakhari, S. and Wanatabe, T. (1977)

Non-Fluorinated propellants and Solvents for Aerosols.

CRC Press, Cleveland, Ohio.

6. Clark, D.G. and Tinson, D.J. (1982)

Acute Inhalation Toxicity of some Halogenated and Non-Halogenated Hydrocarbons.

Human Toxicol. Vol. 1, pp 239-247.

7. CMA (1999)

Robust summary of information on Group 1: High butadiene C4

- 8. CRC Handbook of Chemistry and Physics, 10th Edition. (1990-1991)
- 9. EU (1999)

Draft environmental and health risk assessment of Butadiene.

10. Fuerst, R. and Stephens, S. (1970)

Studies of effects of gases and gamma irradiation on Neurospora crassa

Dev. Ind. Microbiol. Vol. 11, pp 301-310

11. Gas Processors Association (1996)

Table of Physical Constants of paraffin Hydrocarbons and Other Components of Natural Gas.

Gas Processors Association standard 2145-96

12. Grant, W.M. (1974)

Toxicology of the eye, 2nd edition. Charles C. Thomas, Springfield, Ill.

13. Ikoma, T. (1972)

Nichidai Igaku Zasshi, Vol. 31 No. 2. pp 71-

14. Kirwin, C.J and Thomas, W.C. (1980)

In vitro microbiological mutagenicity studies of hydrocarbon propellants.

J. Soc. Cosmet. Chem. Vol. 31., pp 367-370

15. Krantz, J.C., Carr, J. and Vitcha, J.F. (1948)

Anesthesia XXXI. A study of cyclic and non cyclic hydrocarbons on cardiac automaticity.

J. Pharm. Exp. Therap. Vol 94, pp 315-318

#### 6. References

16. Lewis, R.J. (1992)

Sax's Dangerous Properties of Industrial Materials. Eighth edition, van Nostrand Reinhold, New York

- 17. Log Pow database. Pomona College, 1993
- 18. Mackay, D., Patterson, S. and Shiu, W.Y. (1992) Generic models for evaluating the regional fate of chemicals. Chemosphere Vol. 24, pp 695-717
- 19. Mackerer, C. R. and Galvin, J. B. (1999)

The toxicology of nine light petroleum hydrocarbons
J. Tox. And Env. Health, Vol. 58, Numbers 1-2, September 10-24, 1999

20 McKee, R., Frank, E., Heath, J., Owen, D., Przygoda, R., Trimmer, G. and Whitman, F. (1998) Toxicology of n-Pentane (CAS no. 109-66-0) J. App. Toxicol. Vol. 18,pp431-442

21 O'Brien, W.E. and Brown, L.R. (1967)

The catabolism of isobutane and other alkanes by a member of the genus Mycobacterium. Dev. Ind. Microbiol. Vol. 9, pp 389-393

22 Rode, L.J. and Foster, J.W. (1965)

Gaseous hydrocarbons and the germination of bacterial spores Microbiology, Vol. 53, pp 31-38

23 Sandmeyer, E.E. (1981)

Aliphatic hydrocarbons

Chapter 45 in Patty's Industrial Hygiene and Toxicology, Third revised edition. Volume 2B Toxicology. Pages 3175-3220. John Wiley & Sons. New York

24 Shugaev, B.B. (1969)

Concentrations of hydrocarbons in tissues as a measure of toxicity. Arch. Environ. Health Vol. 18, pp 878-882

25 Stephens, S., De Sha, C. and Fuerst, R. (1971)

Phenotypic and genetic effects in Neurospora crassa produced by selected gases and gases mixed with oxygen.

Dev. Ind. Microbiol. Vol. 12, pp 346-353

26 Stewart, R.D. Herrmann, A.A., Baretta, E.D., Forster, H.V, Sikora, J.J., Newton, P.E. and Soto, R. J. (1977)

Acute and repetetive human exposure to isobutane.

Scand. J. Work Environ. & Health Vol. 3, No. 4, pp 234-243

27 van Zandt, P.T.J and van Leeuwen, C.J. (1992)

A proposal for priority setting of existing chemical substances.

Report prepared for the European Commission.

28 Vestal, J.R. and Perry, J.J. (1970)

Effect of substrate on the lipids of the hydrocarbon-utilizing *Mycobacterium vaccae* Can. J. Microbiol., vol. 17, pp 445-449

29 Wanatabe, K. and Takesue, S. (1971)

Effect of some hydrocarbon gases on egg white lysosyme activities on different substrates Enzymologia, Vol. 41, pp 99-111

15 August 2000 6. References€

30 ZoBell, C.E. (1963)

The occurence, effects and fate of oil polluting the sea. Int. J. Air Wat. poll. Pergamon Press Vol. 7, pp 173-198.